

## Search Results

### Feedback Form (Optional)



Scientific & Technical Information Center

The search results generated for your recent request are attached. If you have any questions or comments (compliments or complaints) about the scope or the results of the search, please contact *the EIC searcher* who conducted the search or contact:

Kathleen Fuller, Team Leader, 308-4290, CP3/4 3D62

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#### Voluntary Results Feedback Form

➤ I am an examiner in Workgroup:  Example:

➤ Relevant prior art found, search results used as follows:

- ☐ 102 rejection
- ☐ 103 rejection
- ☐ Cited as being of interest.
- ☐ Helped examiner better understand the invention.
- ☐ Helped examiner better understand the state of the art in their technology.

*Types of relevant prior art found:*

- ☐ Foreign Patent(s)
- ☐ Non-Patent Literature  
(journal articles, conference proceedings, new product announcements etc.)

➤ Relevant prior art not found:

- ☐ Results verified the lack of relevant prior art (helped determine patentability).
- ☐ Search results were not useful in determining patentability or understanding the invention.

**Other Comments:**

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Drop off completed forms in CP3/4 - 3D62.

=> FILE REG

FILE 'REGISTRY' ENTERED AT 10:17:43 ON 02 APR 2002  
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STRUCTURE FILE UPDATES: 31 MAR 2002 HIGHEST RN 403640-18-6  
DICTIONARY FILE UPDATES: 31 MAR 2002 HIGHEST RN 403640-18-6

TSCA INFORMATION NOW CURRENT THROUGH July 7, 2001

Please note that search-term pricing does apply when  
conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Calculated physical property data is now available. See HELP PROPERTIES  
for more information. See STNote 27, Searching Properties in the CAS  
Registry File, for complete details:  
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

The P indicator for Preparations was not generated for all of the  
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12/27/01 and 1/23/02. Use of the P indicator in online and SDI searches  
during this period, either directly appended to a CAS Registry Number  
or by qualifying an L-number with /P, may have yielded incomplete results.  
As of 1/23/02, the situation has been resolved. Also, note that searches  
conducted using the PREP role indicator were not affected.

Customers running searches and/or SDIs in the H/Z/CA/CAPLUS files  
incorporating CAS Registry Numbers with the P indicator between 12/27/01  
and 1/23/02, are encouraged to re-run these strategies. Contact the  
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worldwide, or send an e-mail to [help@cas.org](mailto:help@cas.org) for further assistance or to  
receive a credit for any duplicate searches.

=> FILE HCAPLUS

FILE 'HCAPLUS' ENTERED AT 10:17:49 ON 02 APR 2002  
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FILE COVERS 1907 - 2 Apr 2002 VOL 136 ISS 14  
FILE LAST UPDATED: 30 Mar 2002 (20020330/ED)

This file contains CAS Registry Numbers for easy and accurate  
substance identification.

CAS roles have been modified effective December 16, 2001. Please

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check your SDI profiles to see if they need to be revised. For information on CAS roles, enter HELP ROLES at an arrow prompt or use the CAS Roles thesaurus (/RL field) in this file.

The P indicator for Preparations was not generated for all of the CAS Registry Numbers that were added to the CAS files between 12/27/01 and 1/23/02. As of 1/23/02, the situation has been resolved. Searches and/or SDIs in the H/Z/CA/CAplus files incorporating CAS Registry Numbers with the P indicator executed between 12/27/01 and 1/23/02 may be incomplete. See the NEWS message on this topic for more information.

=> D QUE L16

L3 24 SEA FILE=REGISTRY ABB=ON (10043-35-3/BI OR 106-69-4/BI OR 107-21-1/BI OR 107-41-5/BI OR 107-88-0/BI OR 111-29-5/BI OR 25265-71-8/BI OR 463-79-6/BI OR 50-70-4/BI OR 54289-82-6/BI OR 57-55-6/BI OR 64-17-5/BI OR 67-63-0/BI OR 71-23-8/BI OR 71-36-3/BI OR 7440-21-3/BI OR 7440-56-4/BI OR 7601-90-3/BI OR 7631-86-9/BI OR 7664-39-3/BI OR 7664-93-9/BI OR 7697-37-2/BI OR 7782-99-2/BI OR 78-83-1/BI)

L4 17 SEA FILE=REGISTRY ABB=ON L3 AND OL

L8 acids in claim 6 SEA FILE=REGISTRY ABB=ON SULFURIC ACID/CN OR BORIC ACID/CN OR CARBONIC ACID/CN OR PERCHLORIC ACID/CN OR SULFURIC ACID/CN > b

L9 14 SEA FILE=REGISTRY ABB=ON L4 NOT (1/S OR 1/SI) - alcohols

L10 5 SEA FILE=REGISTRY ABB=ON NITRIC ACID/CN OR PHOSPHORIC ACID/CN OR HYDROCHLORIC ACID/CN OR HYDROFLUORIC ACID/CN OR HYDROBROMIC ACID/CN > c

L11 222913 SEA FILE=HCAPLUS ABB=ON L9 alcohols

L12 96226 SEA FILE=HCAPLUS ABB=ON L8  $H_2SO_4$ ,  $H_3PO_3$ ,  $H_2CO_3$ ,  $HClO_4$ ,  $H_2SO_3$  on  $HBr$

L13 151500 SEA FILE=HCAPLUS ABB=ON L10  $HNO_3$  on  $H_3PO_4$  on  $HCl$  on  $HF$  on  $HBr$

L14 1478 SEA FILE=HCAPLUS ABB=ON L11 AND L12 AND L13

L15 105 SEA FILE=HCAPLUS ABB=ON L14 AND ?ETCH?

L16 14 SEA FILE=HCAPLUS ABB=ON L15 AND (COMPNS OR COMPOSITION?)

=> D L16 ALL 1-14 HITSTR

L16 ANSWER 1 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 2002:143137 HCAPLUS

DN 136:209068

TI **Etching compositions** for selective chemical mechanical planarization of copper, tantalum and tantalum nitride

IN Zhang, Fan; Towery, Daniel L.; Levert, Joseph A.; Mukherjee, Shyama P.

PA USA

SO U.S. Pat. Appl. Publ., 10 pp., Cont. of U.S. Ser. No. 357,264.

CODEN: USXXCO

DT Patent

LA English

IC ICM H01B001-00

NCL 252500000

CC 76-3 (Electric Phenomena)

Section cross-reference(s): 66

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2002020833	A1	20020221	US 2000-745266	20001220
PRAI	US 1999-357264	A1	19990719		
AB	Formulations contg. oxidizing agents and coreactants are given for chem. mech. planarization or spin etch planarization of surfaces of Cu, Ta and TaN. The chem. formulations may optionally include abrasive particles which may be coated with a chem. reactive species. Contact or				

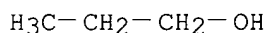
- noncontact CMP may be performed with the present chem. formulations. Substantially 1:1 removal rate selectivity for Cu and Ta/TaN is achieved. Preferred **compsns.** contain H<sub>3</sub>PO<sub>4</sub> 50-70, acetic acid 24-40, and HNO<sub>3</sub> 3-10 vol. parts and optionally 1-15 vol. parts concd. HF.
- ST chem mech planarization **compn** selective copper tantalum nitride; oxidant coreactant **etching compn** planarization copper tantalum nitride
- IT Alcohols, processes  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(aliph.; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Surfactants  
(anionic; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Surfactants  
(cationic; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Polishing  
(chem.-mech., planarization; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Carboxylic acids, processes  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(dicarboxylic; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Abrasives  
**Etching**  
Integrated circuits  
Oxidizing agents  
Stabilizing agents  
Wetting agents  
(**etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Amines, processes  
Glycols, processes ✓  
Phenols, processes  
Transition metal salts  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(**etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Hydrocarbons, processes  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(fluoro, surfactants; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Surfactants  
(nonionic; **etching comps.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)
- IT Borides  
Carbides  
Fluorides, processes  
Hydroxides (inorganic)  
Metals, processes  
Nitrides  
Oxides (inorganic), processes  
Polymers, processes  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical,

- engineering or chemical process); PROC (Process); USES (Uses)  
 (particles; **etching compns.** for selective chem.  
 mech. planarization of copper, tantalum and tantalum nitride)
- IT 1306-38-3, Cerium oxide (CeO<sub>2</sub>), processes  
 RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical,  
 engineering or chemical process); PROC (Process); USES (Uses)  
 (abrasive particle coating; **etching compns.** for  
 selective chem. mech. planarization of copper, tantalum and tantalum  
 nitride)
- IT 64-19-7, Acetic acid, processes 67-56-1, Methanol, processes  
 71-23-8, Propanol, processes 87-69-4, Tartaric acid 88-27-7,  
 2,6-Di-tert-butyl-4[(dimethylamino)methyl]phenol 107-21-1,  
 Ethylene glycol, processes 119-47-1, Agidol-2 144-62-7, Oxalic acid,  
 processes 288-36-8, 1,2,3-Triazole 288-88-0, 1H-1,2,4-Triazole  
 288-94-8, 1H-Tetrazole 1303-96-4, Borax 1310-73-2, Sodium hydroxide,  
 processes 1319-77-3D, Hydroxytoluene, butylated 6915-15-7, Malic acid  
 7647-01-0, Hydrogen chloride, processes 7664-38-2,  
 Phosphoric acid, processes 7664-39-3, Hydrogen fluoride,  
 processes 7664-93-9, Sulfuric acid, processes 7697-37-2  
 , Nitric acid, processes 7727-54-0, Ammonium peroxydisulfate  
 ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) 7733-02-0, Zinc sulfate (ZnSO<sub>4</sub>)  
 RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical,  
 engineering or chemical process); PROC (Process); USES (Uses)  
 (**etching compns.** for selective chem. mech.  
 planarization of copper, tantalum and tantalum nitride)
- IT 7440-25-7, Tantalum, processes 7440-50-8, Copper, processes  
 12033-62-4, Tantalum nitride (TaN)  
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical  
 process); PYP (Physical process); REM (Removal or disposal); TEM  
 (Technical or engineered material use); PROC (Process); USES (Uses)  
 (**etching compns.** for selective chem. mech.  
 planarization of copper, tantalum and tantalum nitride)
- IT 50-21-5, Lactic acid, uses 57-55-6, Propylene glycol, uses  
 60-00-4, EDTA, uses 62-76-0, Sodium oxalate 64-17-5, Ethanol,  
 uses 68-04-2, Trisodium citrate 75-89-8 77-92-9, Citric acid, uses  
 89-65-6, Erythorbic acid 95-14-7, 1H-Benzotriazole 102-71-6,  
 Triethanolamine, uses 104-75-6, 2-Ethylhexylamine 1310-58-3, Potassium  
 hydroxide (KOH), uses 1333-39-7, Phenolsulfonic acid 1336-21-6,  
 Ammonium hydroxide ((NH<sub>4</sub>)(OH)) 1344-28-1, Alumina, uses 3251-23-8,  
 Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) 7439-98-7D, Molybdenum, salts 7440-25-7D,  
 Tantalum, salts 7440-50-8D, Copper, salts 7447-39-4, Copper chloride  
 (CuCl<sub>2</sub>), uses 7447-40-7, Potassium chloride (KCl), uses 7492-68-4,  
 Copper carbonate 7631-86-9, Silica, uses 7631-99-4, Sodium nitrate,  
 uses 7705-08-0, Iron chloride (FeCl<sub>3</sub>), uses 7722-84-1, Hydrogen  
 peroxide, uses 7758-89-6, Copper chloride (CuCl) 7758-98-7, Copper  
 sulfate (CuSO<sub>4</sub>), uses 7772-99-8, Tin chloride (SnCl<sub>2</sub>), uses 7775-09-9,  
 Sodium chlorate (NaClO<sub>3</sub>) 7775-27-1, Sodium peroxydisulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>)  
 8061-51-6, Sodium lignosulfonate 9002-89-5, Polyvinyl alcohol  
 9002-92-0, Poly(oxyethylene)lauryl ether 12125-01-8, Ammonium fluoride  
 (NH<sub>4</sub>F) 14104-77-9, Iron nitrate 16731-55-8, Potassium pyrosulfite  
 (K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) 17084-08-1, Hexafluorosilicate 26053-72-5, Diphenylsulfamic  
 acid 27846-09-9, Iron chloride (FeCl) 31247-73-1, Ammonium copper  
 chloride ((NH<sub>4</sub>)CuCl<sub>3</sub>)  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (**etching compns.** for selective chem. mech.  
 planarization of copper, tantalum and tantalum nitride)
- IT 9004-32-4  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (gelatinized; **etching compns.** for selective chem.  
 mech. planarization of copper, tantalum and tantalum nitride)

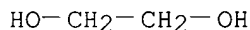
IT 463-79-6D, Carbonic acid, salts  
 RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
 (particles; **etching compns.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)

IT 71-23-8, Propanol, processes 107-21-1, Ethylene glycol, processes 7647-01-0, Hydrogen chloride, processes 7664-38-2, Phosphoric acid, processes 7664-39-3, Hydrogen fluoride, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes  
 RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
 (**etching compns.** for selective chem. mech. planarization of copper, tantalum and tantalum nitride)

RN 71-23-8 HCAPLUS  
 CN 1-Propanol (9CI) (CA INDEX NAME)



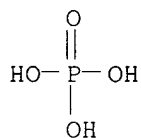
RN 107-21-1 HCAPLUS  
 CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



RN 7647-01-0 HCAPLUS  
 CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



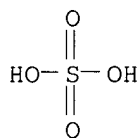
RN 7664-38-2 HCAPLUS  
 CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



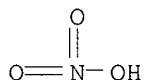
RN 7664-39-3 HCAPLUS  
 CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)



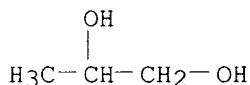
RN 7664-93-9 HCAPLUS  
 CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



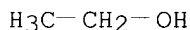
RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



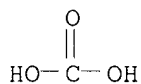
IT 57-55-6, Propylene glycol, uses 64-17-5, Ethanol, uses  
RL: TEM (Technical or engineered material use); USES (Uses)  
(**etching compns.** for selective chem. mech.  
planarization of copper, tantalum and tantalum nitride)  
RN 57-55-6 HCAPLUS  
CN 1,2-Propanediol (8CI, 9CI) (CA INDEX NAME)



RN 64-17-5 HCAPLUS  
CN Ethanol (9CI) (CA INDEX NAME)



IT 463-79-6D, Carbonic acid, salts  
RL: CPS (Chemical process); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(particles; **etching compns.** for selective chem.  
mech. planarization of copper, tantalum and tantalum nitride)  
RN 463-79-6 HCAPLUS  
CN Carbonic acid (7CI, 8CI, 9CI) (CA INDEX NAME)



L16 ANSWER 2 OF 14 HCAPLUS COPYRIGHT 2002 ACS *uses H<sub>2</sub>O*  
AN 2001:421781 HCAPLUS  
DN 135:186791  
TI Stable Surface Coating of Gallium Arsenide with Octadecylthiol Monolayers  
AU Adlkofer, Klaus; Tanaka, Motomu  
CS Lehrstuhl fuer Biophysik E22, Technische Universitaet Muenchen, Garching,  
D-85748, Germany  
SO Langmuir (2001), 17(14), 4267-4273

CODEN: LANGD5; ISSN: 0743-7463

PB American Chemical Society

DT Journal

LA English

CC 72-2 (Electrochemistry)

Section cross-reference(s): 66, 74, 76

AB The authors describe the deposition of octadecylthiol (ODT) monolayers on highly doped n-GaAs electrode surfaces, which showed high stability both in air and in aq. electrolytes. In the 1st part of this study, four different wet chem. **etching** procedures were studied to optimize surface treatment before ODT deposition. The chem. **compn.** of the surface was evaluated by XPS, demonstrating that the photochem. **etching** procedure (called **etch P** in this study) can generate a surface enriched with arsenides, which can serve as the binding sites for sulfides. In the 2nd part of this study, the surface prepd. by **etch P** was coated with an ODT monolayer. The monolayer showed high stability in air, as indicated by the const. ellipsometric thickness. In electrolytes, the stability of the monolayer-coated surface was verified by impedance spectroscopy under zero-current potential ( $U_j=0 = -360$  mV) for  $>10$  h; then the stability of the interface was monitored under different bias potentials. Electrochem. passivation of the GaAs surface was demonstrated for the 1st time under physiol. conditions (in aq. electrolyte, near neutral pH), which allows for the application of GaAs electrodes to biol. systems.

ST stable surface coating gallium arsenide octadecylthiol self assembled monolayer; impedance octadecylthiol self assembled monolayer gallium arsenide; capacitance potential relationship self assembled monolayer octadecylthiol gallium arsenide; **etching** chem photochem gallium arsenide octadecylthiol monolayer deposition

IT Passivation

(electrochem.; of GaAs in aq. neutral electrolytes: stable surface coating of gallium arsenide with octadecylthiol monolayers)

IT Coating materials

(octadecylthiol on GaAs)

IT Electric capacitance-potential relationship

Flatband potential

(of GaAs with octadecylthiol self assembled monolayers)

IT Binding energy

Electric impedance

Equivalent electric circuits

X-ray photoelectron spectra

(of GaAs with octadecylthiol self assembled monolayers and effect of surface pretreatment)

IT **Etching**

(of gallium arsenide in concd. HCl and in HCl/EtOH or H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O prior to octadecylthiol self assembled monolayer deposition on GaAs)

IT Thickness

(of octadecylthiol self assembled monolayers on GaAs)

IT **Etching**

(photochem.; of gallium arsenide in aq. HCl soln. prior to self assembled monolayer deposition on GaAs)

IT Self-assembled monolayers

(stable surface coating of gallium arsenide with octadecylthiol self-assembled monolayers)

IT 64-17-5, Ethanol, uses 7664-93-9, Sulfuric acid, uses

7722-84-1, Hydrogen peroxide, uses

RL: NUU (Other use, unclassified); PRP (Properties); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)

uses H<sub>2</sub>O **(etching** of gallium arsenide in concd. HCl and in HCl/EtOH or H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O prior to octadecylthiol self assembled monolayer



deposition on GaAs)

- IT 7647-01-0, Hydrogen chloride, uses  
 RL: NUU (Other use, unclassified); PRP (Properties); USES (Uses)  
 (photochem. **etching** of gallium arsenide in aq. HCl soln.  
 prior to octadecylthiol self assembled monolayer deposition on GaAs)
- IT 1303-00-0, Gallium Arsenide, properties 2885-00-9, Octadecylthiol  
 RL: PEP (Physical, engineering or chemical process); PRP (Properties);  
 PROC (Process)  
 (stable surface coating of gallium arsenide with octadecylthiol self  
 assembled monolayers in air and in aq. electrolytes)

RE.CNT 49 THERE ARE 49 CITED REFERENCES AVAILABLE FOR THIS RECORD

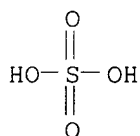
RE

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 Langmuir-Blodgett to Self-Assembly 1991
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 IT 64-17-5, Ethanol, uses 7664-93-9, Sulfuric acid, uses  
 RL: NUU (Other use, unclassified); PRP (Properties); RCT (Reactant); RACT  
 (Reactant or reagent); USES (Uses)  
 (etching of gallium arsenide in concd. HCl and in HCl/EtOH or  
 H2O2-H2SO4-H2O prior to octadecylthiol self assembled monolayer  
 deposition on GaAs)  
 RN 64-17-5 HCAPLUS  
 CN Ethanol (9CI) (CA INDEX NAME)

H<sub>3</sub>C-CH<sub>2</sub>-OH

RN 7664-93-9 HCAPLUS  
 CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



IT 7647-01-0, Hydrogen chloride, uses  
 RL: NUU (Other use, unclassified); PRP (Properties); USES (Uses)  
 (photochem. etching of gallium arsenide in aq. HCl soln.  
 prior to octadecylthiol self assembled monolayer deposition on GaAs)  
 RN 7647-01-0 HCAPLUS  
 CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

HCl

X L16 ANSWER 3 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
 AN 2001:64307 HCAPLUS  
 DN 134:124734  
 TI Compositions and processes for spin etch planarization  
 in semiconductor device fabrication  
 IN Levert, Joseph; Towery, Daniel L.  
 PA Alliedsignal Inc., USA  
 SO PCT Int. Appl., 38 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM H01L021-321  
 ICS C23F003-06  
 CC 76-3 (Electric Phenomena)  
 FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001006555	A1	20010125	WO 2000-US18723	20000710

W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE,  
 DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG,  
 KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX,

NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,  
 UA, UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM  
 RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY,  
 DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ,  
 CF, CG, CI, CM, CA, GN, GW, ML, MR, NE, SN, TD, TG

X US 2001054706 AM 20011227 US 1999-356487 19990719  
 PRAI US 1999-356487 A 19990719

- AB The present invention describes methods and chem. **compns.** for the spin **etch** planarization of surfaces, particularly Cu and Ta. An **etching** soln. is brought into contact with the upper face of a spinning wafer through a nozzle, preferably an oscillating nozzle. The **etching** soln. has a **compn.** that oxidizes the spinning surface, forming a passivation layer thereon. The **etching** soln. further contains reactants for removing the passivation layer exposing the underlying surface to further reaction, leading to the desired **etching** of the surface. The characteristics of the **etching** soln. are adjusted such that reactant diffusion to lower regions of the surface limits the rate of **etching**. Faster reaction occurs at higher regions of the surface lying in more rapidly moving **etching** soln. resulting in the desired planarization.
- ST spin **etching** polishing semiconductor device fabrication; chem mech polishing device fabrication; oxidn **etching** device fabrication
- IT Alcohols, processes  
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
 (aliph.; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Surfactants  
 (anionic; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Surfactants  
 (cationic; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Polishing  
 (chem.-mech.; **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT **Etching**  
 Integrated circuits  
 Semiconductor device fabrication  
 (**compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Hydrocarbons, processes  
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
 (fluoro; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Nozzles  
 (for spin **etch** planarization in semiconductor device fabrication)
- IT Oxidizing agents  
 Wetting agents  
 (in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)
- IT Amines, processes  
 Carboxylic acids, processes  
 Gelatins, processes  
 Phenols, processes  
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)

IT Passivation  
(in spin **etch** planarization in semiconductor device fabrication)

IT Surfactants  
(nonionic; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)

IT Surfactants  
(org.; in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)

IT **Etching**  
(photochem.; for planarization in semiconductor device fabrication)

IT Oxidation  
(surface; in spin **etch** planarization in semiconductor device fabrication)

IT 7440-25-7, Tantalum, processes 7440-50-8, Copper, processes  
RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(**compns.** and processes for spin **etch** planarization of)

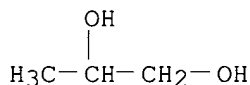
IT 57-55-6, Propyleneglycol, processes 60-00-4, EDTA, processes 62-76-0, Sodium oxalate 64-17-5, Ethanol, processes 64-19-7, Acetic acid, processes 67-56-1, Methanol, processes 68-04-2, Trisodium citrate 71-23-8, n-Propanol, processes 75-89-8 77-92-9, Citric acid, processes 87-69-4, Tartaric acid, processes 88-27-7, 2,6-Di-tert-butyl-4-[(dimethylamino)methyl]phenol 89-65-6, Erythorbic acid 95-14-7, 1H-Benzotriazole 102-71-6, Triethanolamine, processes 104-75-6, 2-Ethylhexylamine 107-21-1, 1,2-Ethanediol, processes 128-37-0, Agidol, processes 139-33-3 144-62-7, Oxalic acid, processes 288-36-8, 1,2,3-Triazole 288-88-0, 1H-1,2,4-Triazole 288-94-8, 1H-Tetrazole 1303-96-4, Borax 1310-73-2, Sodium hydroxide, processes 1333-39-7, Phenolsulfonic acid 1336-21-6, Ammonium hydroxide 6915-15-7, Malic acid 7439-98-7D, Molybdenum, salts, processes 7440-25-7D, Tantalum, salts, processes 7440-50-8D, Copper, salts, processes 7447-40-7, Potassium chloride, processes 7631-95-0, Sodium molybdate 7631-99-4, Sodium nitrate, processes 7647-01-0, Hydrogen chloride, processes 7664-38-2, Phosphoric acid, processes 7664-39-3, Hydrogen fluoride, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes 7722-84-1, Hydrogen peroxide, processes 7733-02-0, Zinc sulfate 7758-89-6, Cuprous chloride 7758-98-7, Cupric sulfate, processes 7775-09-9, Sodium chlorate (NaClO3) 8061-51-6, Sodium lignosulfonate 9002-89-5, Polyvinyl alcohol 9002-92-0, Poly(oxyethylene)lauryl ether 9004-32-4, Carboxymethylcellulose 12125-01-8, Ammonium fluoride 14066-19-4, Monohydrogen phosphate, processes 14265-44-2, Phosphate, processes 16887-00-6, Chloride, processes 17084-08-1, Hexafluorosilicate 26053-72-5, Diphenylsulfamic acid 27846-09-9, Iron monochloride 89800-24-8, Laprol 602  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(in **compns.** and processes for spin **etch** planarization in semiconductor device fabrication)

RE.CNT 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD

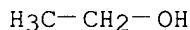
RE

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- (2) Contolini; US 5486234 A 1996 HCAPLUS
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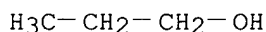
(6) Samsung Electronics; DE 19928570 A 1999 HCAPLUS  
 (7) Sasaki; US 5770095 A 1998 HCAPLUS  
 (8) Sez Semiconductor-Equipment; EP 0905754 A 1999 HCAPLUS  
 (9) Ube Ind Ltd; JP 08236615 A 1996 HCAPLUS  
 (10) Unvala; JOURNAL OF THE ELECTROCHEMICAL SOCIETY 1972, V119(3), P318 HCAPLUS  
 IT 57-55-6, Propyleneglycol, processes 64-17-5, Ethanol,  
 processes 71-23-8, n-Propanol, processes 107-21-1,  
 1,2-Ethanediol, processes 7647-01-0, Hydrogen chloride,  
 processes 7664-38-2, Phosphoric acid, processes  
 7664-39-3, Hydrogen fluoride, processes 7664-93-9,  
 Sulfuric acid, processes 7697-37-2, Nitric acid, processes  
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical  
 process); PROC (Process); USES (Uses)  
 (in **compns.** and processes for spin **etch**  
 planarization in semiconductor device fabrication)  
 RN 57-55-6 HCAPLUS  
 CN 1,2-Propanediol (8CI, 9CI) (CA INDEX NAME)



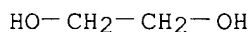
RN 64-17-5 HCAPLUS  
 CN Ethanol (9CI) (CA INDEX NAME)



RN 71-23-8 HCAPLUS  
 CN 1-Propanol (9CI) (CA INDEX NAME)



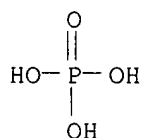
RN 107-21-1 HCAPLUS  
 CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



RN 7647-01-0 HCAPLUS  
 CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



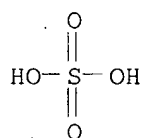
RN 7664-38-2 HCAPLUS  
 CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



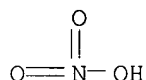
RN 7664-39-3 HCAPLUS  
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



L16 ANSWER 4 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
AN 2000:725881 HCAPLUS  
DN 133:289930  
TI Selective **etching** of doped from undoped polysilicon in  
semiconductor device fabrication  
IN Mercaldi, Garry A.; Yates, Donald L.  
PA Micron Technology, Inc., USA  
SO PCT Int. Appl., 31 pp.  
CODEN: PIXXD2  
DT Patent  
LA English  
IC ICM H01L021-306  
ICS H01L021-3213; C23F001-00  
CC 76-3 (Electric Phenomena)  
Section cross-reference(s): 21  
FAN.CNT 1

*applicants*

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2000060651	A1	20001012	WO 2000-US8939	20000405
W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG,				

KZ, MD, RU, TJ, TM

RW: GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE,  
DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

X US 2001004553 A1 20010621 US 1999-285773 19990405  
EP 1177575 A1 20020206 EP 2000-921671 20000405

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,  
IE, SI, LT, LV, FI, RO

X US 6316370 B1 20011113 US 2000-644699 20000824

PRAI US 1999-285773 A 19990405  
WO 2000-US8939 W 20000405

AB The present invention provides an **etching compn.** which includes a polyhydric alc. in combination with two inorg. acids. Preferably the **etching compn.** of the present invention is a mixt. of a glycol, nitric acid and hydrofluoric acid, with propylene glycol being preferred. The **etching compn.** of the present invention achieves a selectivity of greater than 70:1, doped material to undoped material. The present invention provides an **etching** formulation which has increased selectivity of doped polysilicon to undoped polysilicon and provides an efficient integrated circuit fabrication process without requiring time consuming and costly processing modifications to the **etching** app. or prodn. app.

ST hydric alc inorg acid selective etching doping silicon;  
propylene glycol nitric hydrofluoric acid etching semiconductor device fabrication

IT Densification  
(BSPG; and selective **etching** in semiconductor device fabrication)

IT Annealing  
(and selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT Glycols, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(**etchants**; in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT Borophosphosilicate glasses  
RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)  
(in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT Acids, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(inorg., **etchants**; in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT Alcohols, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(polyhydric, **etchants**; in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT Semiconductor device fabrication  
(selective **etching** of doped from undoped polysilicon in)

IT Doping  
(selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT **Etching**  
(selective; of doped from undoped polysilicon in semiconductor device fabrication)

IT 7440-56-4, Germanium, processes

propylene glycol  
HIV<sub>3</sub>  
1+1=

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)  
(doped; selective **etching** of)

IT 50-70-4, Sorbitol, processes 57-55-6, Propylene glycol, processes 64-17-5, Ethanol, processes 67-63-0, Isopropanol, processes 71-23-8, Propanol, processes 71-36-3, n-Butanol, processes 78-83-1, Iso-butanol, processes 106-69-4, 1,2,6-Hexanetriol 107-21-1, Ethylene glycol, processes 107-41-5, Hexylene glycol 107-88-0, Butylene glycol 111-29-5, 1,5-Pentanediol 463-79-6, Carbonic acid, processes 7601-90-3, Perchloric acid, processes 7664-39-3, Hydrofluoric acid, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes 7782-99-2, Sulfurous acid, processes 10043-35-3, Boric acid, processes 25265-71-8, Dipropylene glycol 54289-82-6

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(**etchants**; in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT 7631-86-9, Silica, processes

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)

(in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

IT 7440-21-3, Silicon, processes

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)

(polycryst.; selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

RE.CNT 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Anon; PATENT ABSTRACTS OF JAPAN 1984, V008(058), PP-261
- (2) Anon; PATENT ABSTRACTS OF JAPAN 1993, V017(681), PP-1660
- (3) Baeslack, W; MATERIALS CHARACTERIZATION 1993, V31(4), P197 HCAPLUS
- (4) Holoubek Jiri Ing; CS 272371 B 1991 HCAPLUS
- (5) Kogyo Gijutsuin; JP 58207009 A 1983 HCAPLUS *HBr<sup>x</sup>, HNO<sub>3</sub> and alcohol (ie. CH<sub>3</sub>OH, EtOH)*
- (6) Sez Semiconduct Equip Zubehoer; EP 0905754 A 1999 HCAPLUS *planarization*
- (7) Sumitomo Metal Ind Ltd; JP 05231996 A 1993 *HF + HNO<sub>3</sub> + glycine*
- (8) Takeuchi Hiroshi; US 5017513 A 1991 HCAPLUS *H<sub>2</sub>PO<sub>4</sub> and HF and alcohol, col 57, lines 24-27*
- (9) Woo, S; US 5518966 A 1996 HCAPLUS *— contain D<sub>2</sub> H<sub>2</sub>O*

IT 50-70-4, Sorbitol, processes 57-55-6, Propylene glycol, processes 64-17-5, Ethanol, processes 67-63-0, Isopropanol, processes 71-23-8, Propanol, processes 71-36-3, n-Butanol, processes 78-83-1, Iso-butanol, processes 106-69-4, 1,2,6-Hexanetriol 107-21-1, Ethylene glycol, processes 107-41-5, Hexylene glycol 107-88-0, Butylene glycol 111-29-5, 1,5-Pentanediol 463-79-6, Carbonic acid, processes 7601-90-3, Perchloric acid, processes 7664-39-3, Hydrofluoric acid, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes 7782-99-2, Sulfurous acid, processes 10043-35-3, Boric acid, processes 25265-71-8, Dipropylene glycol 54289-82-6

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

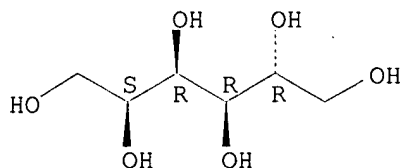
(**etchants**; in selective **etching** of doped from undoped polysilicon in semiconductor device fabrication)

RN 50-70-4 HCAPLUS

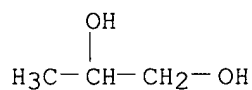
CN D-Glucitol (9CI) (CA INDEX NAME)



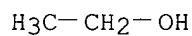
Absolute stereochemistry.



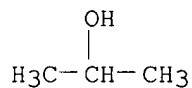
RN 57-55-6 HCAPLUS  
CN 1,2-Propanediol (8CI, 9CI) (CA INDEX NAME)



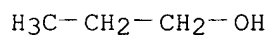
RN 64-17-5 HCAPLUS  
CN Ethanol (9CI) (CA INDEX NAME)



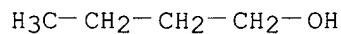
RN 67-63-0 HCAPLUS  
CN 2-Propanol (9CI) (CA INDEX NAME)



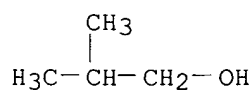
RN 71-23-8 HCAPLUS  
CN 1-Propanol (9CI) (CA INDEX NAME)



RN 71-36-3 HCAPLUS  
CN 1-Butanol (9CI) (CA INDEX NAME)

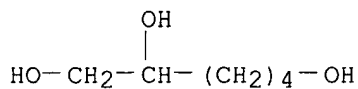


RN 78-83-1 HCAPLUS  
CN 1-Propanol, 2-methyl- (9CI) (CA INDEX NAME)



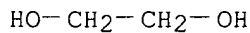
RN 106-69-4 HCAPLUS

CN 1,2,6-Hexanetriol (8CI, 9CI) (CA INDEX NAME)



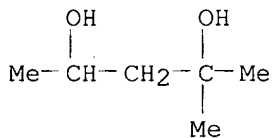
RN 107-21-1 HCAPLUS

CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



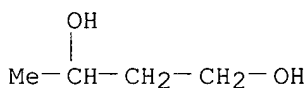
RN 107-41-5 HCAPLUS

CN 2,4-Pentanediol, 2-methyl- (8CI, 9CI) (CA INDEX NAME)



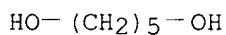
RN 107-88-0 HCAPLUS

CN 1,3-Butanediol (8CI, 9CI) (CA INDEX NAME)



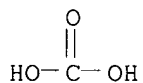
RN 111-29-5 HCAPLUS

CN 1,5-Pentanediol (8CI, 9CI) (CA INDEX NAME)



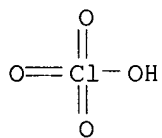
RN 463-79-6 HCAPLUS

CN Carbonic acid (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 7601-90-3 HCAPLUS

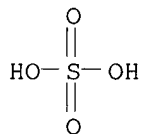
CN Perchloric acid (8CI, 9CI) (CA INDEX NAME)



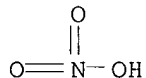
RN 7664-39-3 HCAPLUS  
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

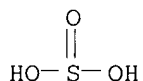
RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



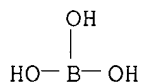
RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



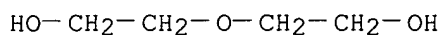
RN 7782-99-2 HCAPLUS  
CN Sulfurous acid (8CI, 9CI) (CA INDEX NAME)



RN 10043-35-3 HCAPLUS  
CN Boric acid (H3BO3) (6CI, 8CI, 9CI) (CA INDEX NAME)

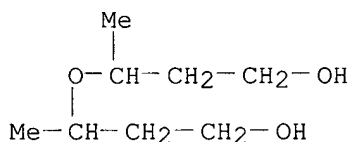


RN 25265-71-8 HCAPLUS  
CN Propanol, oxybis- (9CI) (CA INDEX NAME)



2 ( D1-Me )

RN 54289-82-6 HCAPLUS  
CN 1-Butanol, 3,3'-oxybis- (9CI) (CA INDEX NAME)



L16 ANSWER 5 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 2000:710501 HCAPLUS

133:338496

TL Influence of pre-treatments on the surface condition of 2024-T3 aluminium alloy

Pires, I.; Quintino, L.; Rangel, C. M.; Thompson, G. E.; Skeldon, P.; Zhou, X.

CS Mechanical Engineering Department, Instituto Superior Tecnico, Seccao de Tecnologia Mecanica, Lisbon, 1096, Port.

SO Transactions of the Institute of Metal Finishing (2000), 78(5), 179-185  
CODEN: TIMFA2; ISSN: 0020-2967

PB Institute of Metal Finishing

DT Journal

LA English

CC 56-9 (Nonferrous Metals and Alloys)

AB The influences of various pre-treatments of interest in adhesive bonding on the surface condition of 2024-T3 alloy have been examd. In particular, the morphologies of films formed during alk. **etching** (NaOH), electropolishing (perchloric acid/ethanol), acid pickling (Na2Cr2O7/H2SO4), and anodizing (H3PO4), and the consequences of film growth to the **compn.** of the alloy, have been detd. using TEM, SEM, and Rutherford backscattering spectroscopy. The pre-treatments result generally in scalloped surfaces, with deeper cavities assocd. originally with second phase particles. The topog. of the surface is generated primarily in the pre-treatment stages, with subsequent anodizing having a lesser influence. Enhanced attack of the alloy in the vicinity of grain boundaries occurs during acid pickling, which appears to be accentuated during subsequent anodizing. Alk. **etching** and electropolishing produce compact films, resp. about 5-8 and 2-3 nm thick, on the main alloy surface. In contrast, acid pickling produces an open-textured, porous film, about 30 nm thick and of fibrous appearance in section, with a thin barrier layer at the alloy/film interface. The porous films produced by anodizing in phosphoric acid are of typical thickness in the range 200-350 nm, with a 10-18 nm thick, barrier layer. The formation of the various films results in significant enrichment of copper in the alloy to the range 4.2 .times. 1015 to 6.4 .times. 1015 Cu atoms cm-2.

ST aluminum alloy adhesive bonding surface pretreatment; **etching** pretreatment aluminum alloy adhesive bonding; electropolishing pretreatment aluminum alloy adhesive bonding; pickling pretreatment

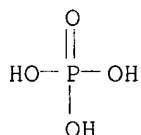
- aluminum alloy adhesive bonding; anodizing pretreatment aluminum alloy adhesive bonding
- IT **Etching**  
(alkyline; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT Adhesive bonding  
(effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT Polishing  
(electrochem., perchloric acid-ethanol; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT Anodization  
(in phosphoric acid; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT Pickling  
(in sodium chromate-sulfuric acid; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT 1310-73-2, Sodium hydroxide, processes  
RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
(alkyline **etching** with; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT **7664-38-2**, Phosphoric acid, processes  
RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
(anodization in; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT 12616-84-1, Aa2024  
RL: PEP (Physical, engineering or chemical process); PRP (Properties); PROC (Process)  
(effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT **64-17-5**, Ethanol, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)  
(electropolishing in perchloric acid-ethanol; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT **7601-90-3**, Perchloric acid, processes  
RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
(electropolishing in perchloric acid-ethanol; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)
- IT **7664-93-9**, Sulfuric acid, processes 10588-01-9, Sodium chromate Na2Cr2O7  
RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
(pickling in sodium chromate-sulfuric acid; effect of pre-treatments on surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)

RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD

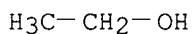
RE

- (1) Buchheit, R; J Electrochem Soc 1997, V144, P2621 HCAPLUS
- (2) Doolittle, L; Nucl Instrum Meth 1985, VB9, P344 HCAPLUS
- (3) Fishkis, M; Wear 1997, V206, P156 HCAPLUS
- (4) Gao, M; Met Mater Trans 1998, V29A, P1145 HCAPLUS
- (5) Habazaki, H; Corros Sci 1996, V38, P1033 HCAPLUS
- (6) Habazaki, H; J Electrochem Soc 1999, V144, P4217

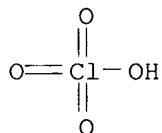
(7) Habazaki, H; Phil Mag 1996, VB 73, P445  
 (8) Habazaki, H; Trans IMF 1997, V75, P18 HCAPLUS  
 (9) Leth-Olsen, H; J Electrochem Soc 1997, V144, PL197  
 (10) Rigney, O; Am Rev Mater Sci 1988, V18, P141  
 (11) Scully, J; Corros Sci 1993, V35, P185 HCAPLUS  
 (12) Thompson, G; Corrosion: Aqueous Processes and Passive Films 1962, P205  
 (13) Venables, J; J Mater Sci 1984, V19, P2431 HCAPLUS  
 (14) Wegman, R; Surface Preparation Techniques for Adhesive Bonding 1989  
 (15) Wei, R; Met Mater Trans 1998, V29A, P1153 HCAPLUS  
 (16) Zhou, X; Corros Sci 1999, V41, P1599 HCAPLUS  
 IT 7664-38-2, Phosphoric acid, processes  
 RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC  
 (Process); RACT (Reactant or reagent)  
 (anodization in; effect of pre-treatments on surface condition of  
 2024-T3 aluminum alloy for subsequent adhesive bonding)  
 RN 7664-38-2 HCAPLUS  
 CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



IT 64-17-5, Ethanol, processes  
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical  
 process); PROC (Process); USES (Uses)  
 (electropolishing in perchloric acid-ethanol; effect of pre-treatments  
 on surface condition of 2024-T3 aluminum alloy for subsequent adhesive  
 bonding)  
 RN 64-17-5 HCAPLUS  
 CN Ethanol (9CI) (CA INDEX NAME)



IT 7601-90-3, Perchloric acid, processes  
 RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC  
 (Process); RACT (Reactant or reagent)  
 (electropolishing in perchloric acid-ethanol; effect of pre-treatments  
 on surface condition of 2024-T3 aluminum alloy for subsequent adhesive  
 bonding)  
 RN 7601-90-3 HCAPLUS  
 CN Perchloric acid (8CI, 9CI) (CA INDEX NAME)

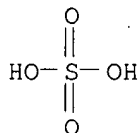


IT 7664-93-9, Sulfuric acid, processes  
 RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC  
 (Process); RACT (Reactant or reagent)  
 (pickling in sodium chromate-sulfuric acid; effect of pre-treatments on

surface condition of 2024-T3 aluminum alloy for subsequent adhesive bonding)

RN 7664-93-9 HCAPLUS

CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



L16 ANSWER 6 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 2000:628404 HCAPLUS

DN 133:201939

TI Method and system to uniformly **etch** substrates using an **etching composition** comprising a fluoride ion source and a hydrogen ion source

IN Christenson, Kurt K.

PA Fsi International, Inc., USA

SO PCT Int. Appl., 35 pp.

CODEN: PIXXD2

DT Patent

LA English

IC ICM H01L021-311

ICS H01L021-306; H01L021-00

CC 76-11 (Electric Phenomena)

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI WO 2000052747	A1	20000908X	WO 2000-US5484	20000302

W: CN, JP, KR

RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

PRAI US 1999-261786 A 19990303

AB The present invention provides methods and a system for uniformly plasma **etching** substrates. Specifically, the method and system of the present invention provide for the nonimmersive contact of the substrate to be **etched** with an **etching compn.** comprising a F- ion source and a H ion source. By using an **etching compn.** comprising such components, not only is the **etching** of traditional substrate materials, i.e., Si oxide, improved, but the **etching** of substrate materials traditionally difficult to **etch** satisfactorily, i.e., Si nitride, is made possible.

ST fluoride hydrogen ion etching app semiconductor device fabrication

IT **Etching**

**Etching apparatus**

Nozzles

Semiconductor device fabrication

Solvents

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

IT Acids, processes

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(method and system to uniformly **etch** substrates using

*contains organic acid CH<sub>3</sub>COOH*

**etching compn.** comprising fluoride ion source and hydrogen ion source)

IT **Etching**

(spray; method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

- IT 56-81-5, Glycerol, processes 64-19-7, Acetic acid, processes 107-21-1, Ethylene glycol, processes 7647-01-0, Hydrogen chloride, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes 7732-18-5, Water, processes 12125-01-8, Ammonium fluoride 12408-02-5, Hydrogen ion, processes 16984-48-8, Fluoride, processes

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

- IT 7664-39-3, Hydrogen fluoride, processes

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent); USES (Uses)

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

- IT 12033-89-5, Silicon nitride, processes

RL: PEP (Physical, engineering or chemical process); RCT (Reactant); TEM (Technical or engineered material use); PROC (Process); RACT (Reactant or reagent); USES (Uses)

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

- IT 7631-86-9, Silicon dioxide, processes

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

RE.CNT 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Christenson, K; SOLID STATE TECHNOLOGY 1997, V40(12), P55 HCAPLUS
- (2) Deckert, C; US 4269654 A 1981 HCAPLUS
- (3) Gaulhofer, E; SOLID STATE TECHNOLOGY 1991, V34(5), P57 HCAPLUS
- ✓(4) Lee, K; WO 9831768 A 1998 HCAPLUS *includes H<sub>2</sub>O*
- ✓(5) Muraoka, H; US 5681398 A 1997 HCAPLUS *- contains H<sub>2</sub>O*
- (6) Park, J; US 5087323 A 1992 *doesn't specify type of etchant*
- (7) Schnegg, A; US 4971654 A 1990 HCAPLUS
- (8) Stmicroelectronics Sa; FR 2769248 A 1999 HCAPLUS
- (9) Ziger, D; US 5472562 A 1995 HCAPLUS *H<sub>3</sub>PO<sub>4</sub>, HF, and HNO<sub>3</sub>; does specify alcohol*

- IT 107-21-1, Ethylene glycol, processes 7647-01-0, Hydrogen chloride, processes 7664-93-9, Sulfuric acid, processes 7697-37-2, Nitric acid, processes

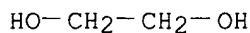
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

RN 107-21-1 HCAPLUS

CN 1,2-Ethanediol (9CI) (CA INDEX NAME)

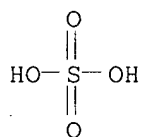




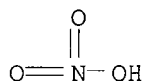
RN 7647-01-0 HCAPLUS  
CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



IT 7664-39-3, Hydrogen fluoride, processes  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent); USES (Uses)  
(method and system to uniformly **etch** substrates using **etching compn.** comprising fluoride ion source and hydrogen ion source)

RN 7664-39-3 HCAPLUS  
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)



X  
uses  
DI  
H<sub>2</sub>O

L16 ANSWER 7 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
AN 1999:21615 HCAPLUS  
DN 130:87970  
TI Method for producing a micro optical semiconductor lens  
IN Tran, Dean; Anderson, Eric R.; Strijek, Ronald L.; Rezek, Edward A.  
PA TRW Inc., USA  
SO U.S., 13 pp.  
CODEN: USXXAM  
DT Patent  
LA English  
IC ICM H01L027-14  
ICS H01L031-0304  
NCL 430321000  
CC 73-11 (Optical, Electron, and Mass Spectroscopy and Other Related Properties)

Section cross-reference(s): 76

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5853960	A	19981229X	US 1998-40636	19980318
	JP 11298046	A2	19991029X	JP 1998-372169	19981228
PRAI	US 1998-40636		19980318		
AB	Methods for fabricating Group III-V semiconductor microlenses for hybrid integration with microoptical devices are described which entail forming lenses from a semiconductor wafer by selectively <b>etching</b> a surface of the semiconductor wafer and forming a lens arm from the semiconductor wafer on a surface opposite the surface by selectively <b>etching</b> the surface of the semiconductor wafer. The lens and lens arm may then be cleaved from the substrate wafer and directly mounted to a microoptical device. The lens may be provided with an antireflective coating and the lens arm may be metalized prior to cleaving. The <b>etching</b> step may be a wet or dry <b>etch</b> . By using a semiconductor material to form the lenses the thermal stability of the integrated systems is enhanced over conventional systems.				
ST	semiconductor microlens prodn				
IT	Dry <b>etching</b> Photoresists Plasma <b>etching</b> Reactive ion <b>etching</b> Selective <b>etching</b> (in semiconductor microlens prodn.)				
IT	Microlenses (semiconductor microlens prodn.)				
IT	Semiconductor device fabrication (semiconductor microlens prodn. in)				
IT	7783-40-6, Magnesium fluoride 13709-52-9, Hafnium fluoride RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses) (antireflective coating contg.; semiconductor microlens prodn.)				
IT	64-19-7, Acetic acid, uses 67-56-1, Methanol, uses 67-63-0, Isopropanol, uses 74-82-8, Methane, uses 74-88-4, Methyl iodide, uses 75-03-6, Ethyl iodide 75-30-9, 2-Iodopropane 75-71-8, Dichlorodifluoromethane 76-16-4, Hexafluoroethane 77-92-9, Citric acid, uses 1333-74-0, Hydrogen, uses 1336-21-6, Ammonium hydroxide 7440-37-1, Argon, uses 7647-01-0, Hydrochloric acid, uses 7664-38-2, Phosphoric acid, uses 7664-39-3, Hydrofluoric acid, uses 7664-93-9, Sulfuric acid, uses 7697-37-2, Nitric acid:, uses 7705-08-0, Iron chloride (FeCl3), uses 7722-84-1, Hydrogen peroxide, uses 7726-95-6, Bromine, uses 7758-05-6 7778-50-9, Potassium dichromate 7782-44-7, Oxygen, uses 7782-50-5, Chlorine, uses 7789-58-4, Iodine bromide (IBr3) 10035-10-6, Hydrobromic acid, uses RL: NUU (Other use, unclassified); USES (Uses) ( <b>etchant</b> contg.; in semiconductor microlens prodn.)				
IT	1344-28-1, Aluminum oxide, uses 7631-86-9, Silicon dioxide, uses 12033-89-5, Silicon nitride, uses RL: DEV (Device component use); NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses) (mask <b>compns.</b> and antireflective coatings contg.; in semiconductor microlens prodn.)				
IT	111-15-9, 2-Ethoxyethylacetate 123-86-4, n-Butyl acetate 999-97-3, Hexamethyldisilazane 1330-20-7, Xylene, uses RL: NUU (Other use, unclassified); USES (Uses) (mask <b>compns.</b> contg.; in semiconductor microlens prodn.)				
IT	7440-06-4, Platinum, uses 7440-32-6, Titanium, uses 7440-57-5, Gold,				

uses

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(metalization; semiconductor microlens prodn.)

IT 1303-00-0, Gallium arsenide, uses 1303-11-3, Indium arsenide, uses 12063-98-8, Gallium phosphide, uses 22398-80-7, Indium phosphide, uses

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(semiconductor microlens prodn.)

RE.CNT 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Anon; JP 07-030082 1995 HCAPLUS

(2) Anon; Appl Phys Lett 1983, V43, P624

(3) Anon; Electronics Letters 1988, V24(2), P109

(4) Anon; IEEE Electronic Components and Technology Conference 1997, P7

(5) Anon; Optical Engineering 1994, V33(11), P3547

(6) Anon; Optical Engineering 1994, V33(11), P3552

(7) Anon; Optical Engineering 1994, V33(11), P3578

(8) Anon; Optical Engineering 1997, V33(11), P1095

(9) Anon; SPIE 1995, V2383, P310

(10) Basavanhally; US 5346583 1994

(11) Brewer; US 5018164 1991

(12) Wakabayshi; US 5316640 1994 HCAPLUS

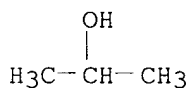
IT 67-63-0, Isopropanol, uses 7647-01-0, Hydrochloric acid, uses 7664-38-2, Phosphoric acid, uses 7664-39-3, Hydrofluoric acid, uses 7664-93-9, Sulfuric acid, uses 7697-37-2, Nitric acid:, uses 10035-10-6, Hydrobromic acid, uses

RL: NUU (Other use, unclassified); USES (Uses)

(etchant contg.; in semiconductor microlens prodn.)

RN 67-63-0 HCAPLUS

CN 2-Propanol (9CI) (CA INDEX NAME)



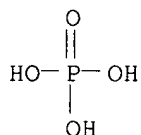
RN 7647-01-0 HCAPLUS

CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

HCl

RN 7664-38-2 HCAPLUS

CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)

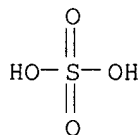


RN 7664-39-3 HCAPLUS

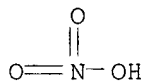
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



RN 10035-10-6 HCAPLUS  
CN Hydrobromic acid (8CI, 9CI) (CA INDEX NAME)

HBr

L16 ANSWER 8 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 1998:813611 HCAPLUS

DN 130:89201

TI Production method of solder bumps for flip-chip mounting of semiconductor device, solder bumps themselves, and their analysis

IN Huh, Nam-Joong; Kwon, Yong-Hwan; Park, Jong-Han

PA Samsung Electronics Co., Ltd., S. Korea

SO Jpn. Kokai Tokkyo Koho, 11 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM H01L021-60

ICS H01L021-60; G01N021-88; H01L023-12

CC 76-3 (Electric Phenomena)

Section cross-reference(s): 79

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10335364	A2	19981218*	JP 1998-47948	19980227
	JP 3004959	B2	20000131*		
	US 6013572	A	20000111*	US 1998-63716	19980421
PRAI	KR 1997-21022	A	19970527		

AB The title method involves forming a boundary film on a semiconductor substrate by a photolithog. method, removing the photoresist used in the photolithog. method from the desired regions of the boundary film, successively plating the regions exposed by the removal with Ag and Sn, completely removing the photoresist, **etching** the boundary film exposed by the complete removal, and reflowing the platings to obtain an

uses DI H<sub>2</sub>O

cols, lines 1-5)

alloy having a desired **compn.** Specifically, the boundary film may comprise a layer of Ti, Cr, and/or Ti-W and a layer of Cu and/or Ni. A method for anal. involves cutting solder bumps to a desired size, and mounting on an epoxy resin to obtain a sample for, e.g., electron microprobe anal.

ST solder bump semiconductor device electron microprobe analysis;  
electroplating photolithog **etching** solder bump

IT **Etching**

Photolithography

(in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT Electroplating

(of silver and titanium in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT Electron microprobe analysis

(of solder bumps for flip-chip mounting of semiconductor device)

IT Solders

(silver and tin; prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT Bump contacts

(solder; prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT 7440-02-0, Nickel, processes 7440-32-6, Titanium, processes 7440-47-3, Chromium, processes 7440-50-8, Copper, processes 12642-02-3

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(boundary film; in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT 67-56-1, Methanol, uses 7647-01-0, Hydrogen chloride, uses

7664-39-3, Hydrogen fluoride, uses 7664-93-9, Sulfuric acid, uses 7697-37-2, Nitric acid, uses 7722-84-1, Hydrogen peroxide, uses

RL: TEM (Technical or engineered material use); USES (Uses)

(**etchant** in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT 67-63-0, Isopropanol, uses

RL: TEM (Technical or engineered material use); USES (Uses)

(for resist removal in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT 7440-22-4, Silver, processes 7440-31-5, Tin, processes

RL: ANT (Analyte); DEV (Device component use); PEP (Physical, engineering or chemical process); ANST (Analytical study); PROC (Process); USES (Uses)

(prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

IT 7647-01-0, Hydrogen chloride, uses 7664-39-3, Hydrogen fluoride, uses 7664-93-9, Sulfuric acid, uses 7697-37-2, Nitric acid, uses

RL: TEM (Technical or engineered material use); USES (Uses)

(**etchant** in prodn. and anal. of solder bumps for flip-chip mounting of semiconductor device)

RN 7647-01-0 HCAPLUS

CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

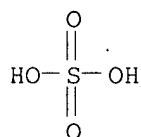
HCl

RN 7664-39-3 HCAPLUS

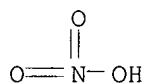
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

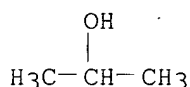
RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



IT 67-63-0, Isopropanol, uses  
RL: TEM (Technical or engineered material use); USES (Uses)  
(for resist removal in prodn. and anal. of solder bumps for flip-chip  
mounting of semiconductor device)  
RN 67-63-0 HCAPLUS  
CN 2-Propanol (9CI) (CA INDEX NAME)



L16 ANSWER 9 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
AN 1998:527177 HCAPLUS  
DN 129:163555  
TI **Composition** for cleaning and **etching** electronic  
display and substrate  
IN Lee, Ke Won  
PA S. Korea  
SO PCT Int. Appl., 36 pp.  
CODEN: PIXXD2  
DT Patent  
LA English  
IC C09K013-04; C03C015-00; C23F001-24; H01L021-306; H01L021-465  
CC 49-11 (Industrial Inorganic Chemicals)  
Section cross-reference(s): 46, 56, 74, 76

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9831768	A1	19980723 ✓	WO 1998-KR11	19980121
	W: CN, JP, US				
	RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	EP 892840	A1	19990127 ✓	EP 1998-901121	19980121
	R: DE, FR, GB, NL				

uses  
DI  
H<sub>2</sub>O

use DI H<sub>2</sub>O

	CN 1216059	A	19990505	CN 1998-800045	19980121
	JP 2000507304	T2	20000613	JP 1998-534157	19980121
	US 6194365	B1	20010227	US 1998-142750	19980915
PRAI	KR 1997-1539	A	19970121		
	KR 1997-53384	A	19971017		
	WO 1998-KR11	W	19980121		

AB This invention relates to a **compn.** for cleaning and **etching** the surface in fabricating electronic displays and the substrates. Specifically this invention relates to a **compn.** to effectively remove the contaminants by cleaning, to remove any contaminants on the surface, and to **etch** SiO<sub>2</sub> and Si substrate in the fabrication process of electronic displays, quartz devices, wafer, and semiconductor wafer. According to this invention, it is possible to clean and **etch** more efficiently and conveniently. Also the surface roughness is improved. Further the **compn.** of this invention can be made available in powder type for prepg. a defined amt. of soln. It provides the conveniences in transportation, handling and storage.

ST electronic display cleaning **etching compn**; quartz device cleaning **etching compn**; **etching** cleaning **compn** semiconductor wafer

IT Cleaning  
(chem.; **compns.** for cleaning and **etching** electronic display and substrate)

IT Detergents  
**Etching**  
Lithography  
Optical imaging devices  
Semiconductor materials  
Surfactants  
(**compns.** for cleaning and **etching** electronic display and substrate)

IT Cast aluminum alloys  
RL: DEV (Device component use); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

IT Fluoro hydrocarbons  
RL: MOA (Modifier or additive use); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

IT Fluorides, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

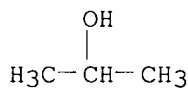
IT Sulfonates  
RL: NUU (Other use, unclassified); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

IT Sulfonic acids, uses  
RL: NUU (Other use, unclassified); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

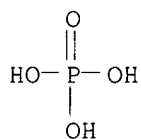
IT 7429-90-5, Aluminum, uses 7440-21-3, Silicon, uses 14808-60-7, Quartz, uses  
RL: DEV (Device component use); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

IT 7631-86-9, Silica, uses  
RL: MOA (Modifier or additive use); USES (Uses)  
(**compns.** for cleaning and **etching** electronic display and substrate)

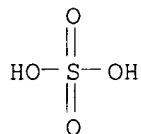
display and substrate)  
 IT 62-76-0, Sodium oxalate 63-74-1, Sulfonyl amide 64-19-7, Acetic acid, uses 67-63-0, 2-Propanol, uses 97-05-2, Sulfosalicylic acid 144-62-7, Oxalic acid, uses 831-54-9, Sodium sulfosalicylate 1333-83-1, Sodium bifluoride 1341-49-7, Ammonium bifluoride 5329-14-6, Sulfamic acid 6009-70-7, Ammonium oxalate monohydrate 6100-20-5 6484-52-2, Ammonium nitrate, uses 6487-48-5, Potassium oxalate monohydrate 7631-99-4, Sodium nitrate, uses 7664-38-2, Phosphoric acid, uses 7664-93-9, Sulfuric acid, uses 7681-49-4, Sodium fluoride, uses 7727-21-1, Potassium persulfate 7727-54-0, Ammonium persulfate 7757-79-1, Potassium nitrate, uses 7773-06-0, Ammonium sulfamate 7775-27-1, Sodium persulfate 7787-32-8, Barium fluoride 7789-23-3, Potassium fluoride 7789-29-9, Potassium bifluoride 10022-31-8, Barium nitrate 12125-01-8, Ammonium fluoride 13826-83-0, Ammonium fluoroborate  
 RL: NUU (Other use, unclassified); USES (Uses)  
 (compns. for cleaning and etching electronic display and substrate)  
 IT 67-63-0, 2-Propanol, uses 7664-38-2, Phosphoric acid, uses 7664-93-9, Sulfuric acid, uses  
 RL: NUU (Other use, unclassified); USES (Uses)  
 (compns. for cleaning and etching electronic display and substrate)  
 RN 67-63-0 HCAPLUS  
 CN 2-Propanol (9CI) (CA INDEX NAME)



RN 7664-38-2 HCAPLUS  
 CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 7664-93-9 HCAPLUS  
 CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



X L16 ANSWER 10 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
 AN 1992:154261 HCAPLUS  
 DN 116:154261  
 TI Acidic liquid composition and process for cleaning aluminum  
 IN Aoki, Tomoyuki; Iino, Yasuo; Ono, Yoji; Asai, Shinichiro



PA Henkel K.-G.a.A., USA  
 SO PCT Int. Appl., 16 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM C23G001-12  
 CC 46-6 (Surface Active Agents and Detergents)  
 Section cross-reference(s): 56

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9119830	A1	19911226	WO 1991-US4263	19910614
	W: AU, BR, CA, US				
	RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE				
	JP 04052289	A2	19920220	JP 1990-160442	19900619
	JP 07122152	B4	19951225		
	CA 2084302	AA	19911220	CA 1991-2084302	19910614
	AU 9180524	A1	19920107	AU 1991-80524	19910614
	AU 646268	B2	19940217		
	EP 533803	A1	19930331	EP 1991-911677	19910614
	EP 533803	B1	19951004		
	R: AT, DE, ES, FR, GB, IT, SE				
	BR 9106557	A	19930601	BR 1991-6557	19910614
	AT 128740	E	19951015	AT 1991-911677	19910614
	ES 2080322	T3	19960201	ES 1991-911677	19910614
	US 5336425	A	19940809	US 1992-971924	19921221
PRAI	JP 1990-160442		19900619		
	WO 1991-US4263		19910614		

one of  
 $H_2SO_4$ ,  $HNO_3$  or  $H_3PO_4$

$H_2O$  and  $H_2O_2$ ,  $H_2SO_4$  and/or  $HNO_3$   
 and glycol(s).

consists of  $H_2O$

AB The title **compn.**, contg. mineral acid, oxidant, polyvalent metal ions, and surfactant and useful for removing smut and scale and **etching** Al and Al alloy surfaces, is stabilized against loss of cleaning power by adding .gtoreq.1 C2-10 glycol. A **compn.** contg.  $H_3PO_4$  6,  $H_2SO_4$  9,  $HNO_3$  1.0,  $Fe^{3+}$  0.05,  $SO_4^{2-}$  0.13,  $H_2O_2$  0.5, propylene glycol (I) 0.5, and nonionic surfactants 2.0 g/L showed surfactant decompn. during 72 h at 75.degree. 15%, vs. 40 without I.

ST phosphoric acid cleaning aluminum; sulfuric acid cleaning aluminum; nitric acid cleaning aluminum; glycol stabilizer acid cleaning aluminum; propylene glycol stabilizer acid cleaning; nonionic surfactant stabilizer acid cleaning

IT Acids, uses  
 RL: USES (Uses)  
 (cleaners contg. nonionic surfactants and, for aluminum, stabilizers for)

IT Stabilizing agents  
 (glycols, for cleaners contg. acids and nonionic surfactants, for aluminum)

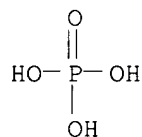
IT **Etching**  
 (of aluminum, acid solns. contg. nonionic surfactants for, stabilizers for)

IT Glycols, uses  
 RL: USES (Uses)  
 (stabilizers, in acid- and nonionic surfactant-contg. cleaners for aluminum)

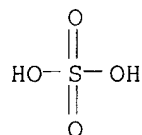
IT Detergents  
 (cleaning **compns.**, acid- and nonionic surfactant-contg., for aluminum, stabilizers for)

IT 9003-11-6D, Ethylene oxide-propylene oxide copolymer, monoalkyl ethers 9016-45-9, Polyethylene glycol mono(nonylphenyl) ether 10028-22-5, Ferric sulfate  
 RL: USES (Uses)

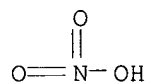
- (cleaners contg. acids and, for aluminum, stabilizers for)
- IT 7664-38-2, Phosphoric acid, miscellaneous 7664-93-9,  
Sulfuric acid, miscellaneous 7697-37-2, Nitric acid,  
miscellaneous  
RL: MSC (Miscellaneous)  
(cleaners contg. nonionic surfactants and, for aluminum, stabilizers  
for)
- IT 7429-90-5, Aluminum, miscellaneous  
RL: MSC (Miscellaneous)  
(cleaners for, acid- and nonionic surfactant-contg., stabilizers for)
- IT 57-55-6, Propylene glycol, uses 107-21-1, Ethylene  
glycol, uses 111-46-6, Diethylene glycol, uses 112-27-6, Triethylene  
glycol  
RL: USES (Uses)  
(stabilizers, for acid- and nonionic surfactant-contg. cleaners for  
aluminum)
- IT 7664-38-2, Phosphoric acid, miscellaneous 7664-93-9,  
Sulfuric acid, miscellaneous 7697-37-2, Nitric acid,  
miscellaneous  
RL: MSC (Miscellaneous)  
(cleaners contg. nonionic surfactants and, for aluminum, stabilizers  
for)
- RN 7664-38-2 HCAPLUS  
CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



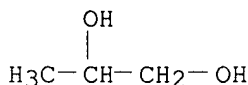
- RN 7664-93-9 HCAPLUS  
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



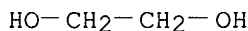
- RN 7697-37-2 HCAPLUS  
CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



- IT 57-55-6, Propylene glycol, uses 107-21-1, Ethylene  
glycol, uses  
RL: USES (Uses)  
(stabilizers, for acid- and nonionic surfactant-contg. cleaners for  
aluminum)
- RN 57-55-6 HCAPLUS  
CN 1,2-Propanediol (8CI, 9CI) (CA INDEX NAME)



RN 107-21-1 HCAPLUS  
CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



L16 ANSWER 11 OF 14 HCAPLUS COPYRIGHT 2002 ACS  
X AN 1990:228025 HCAPLUS  
DN 112:228025  
TI **Etching-ink compositions** for forming transparent  
electrode patterns  
IN Matsuda, Tsutomu  
PA Ricoh Co., Ltd., Japan  
SO Jpn. Kokai Tokkyo Koho, 4 pp.  
CODEN: JKXXAF  
DT Patent  
LA Japanese  
IC ICM C23F001-30  
ICS H01B013-00; H01L021-28; H01L021-308  
CC 76-2 (Electric Phenomena)  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 01147078	A2	19890608	JP 1987-305462	19871202
AB	The title <b>comps.</b> include glycols or their ethers, and an <u>acid</u> or salt which is dissolved or dispersed in the soln., which is acidic. A transparent electrode pattern is prepd. by printing the ink on an inorg. transparent elec. conductive film on a substrate, and <b>etching</b> the printed ink.				
ST	<b>etching</b> ink transparent electrode pattern				
IT	Glycols, uses and miscellaneous				
	RL: TEM (Technical or engineered material use); USES (Uses) ( <b>etching-ink comps.</b> contg., for patterning transparent electrodes)				
IT	Electric conductors (ink <b>comps.</b> for <b>etching</b> of, in forming transparent electrode patterns)				
IT	Ethers, uses and miscellaneous				
	RL: TEM (Technical or engineered material use); USES (Uses) (glycol, <b>etching-ink comps.</b> contg., for patterning transparent electrodes)				
IT	Electrodes (transparent, <b>etching</b> ink <b>comps.</b> for patterning)				
IT	57-55-6, Propylene glycol, uses and miscellaneous 107-21-1 , Ethylene glycol, uses and miscellaneous 111-77-3, Diethyleneglycolmonomethyl ether 471-34-1, Calcium carbonate, uses and miscellaneous 7631-86-9, Silica, uses and miscellaneous 7647-01-0, Hydrochloric acid, uses and miscellaneous 7664-93-9, Sulfuric acid, uses and miscellaneous 7772-99-8, Tin chloride (SnCl <sub>2</sub> ), uses and miscellaneous 9002-89-5, Polyvinylalcohol 13463-67-7, Titanium oxide (TiO <sub>2</sub> ), uses and miscellaneous 25322-68-3,				

limited to one acid

X HCl made  
from  
ZnCl<sub>2</sub> in  
glycol

Polyethylene glycol

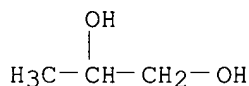
RL: TEM (Technical or engineered material use); USES (Uses)  
(etching-ink compns. contg., for patterning  
transparent electrodes)

IT 57-55-6, Propylene glycol, uses and miscellaneous 107-21-1  
, Ethylene glycol, uses and miscellaneous 7647-01-0,  
Hydrochloric acid, uses and miscellaneous 7664-93-9, Sulfuric  
acid, uses and miscellaneous

RL: TEM (Technical or engineered material use); USES (Uses)  
(etching-ink compns. contg., for patterning  
transparent electrodes)

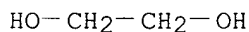
RN 57-55-6 HCAPLUS

CN 1,2-Propanediol (8CI, 9CI) (CA INDEX NAME)



RN 107-21-1 HCAPLUS

CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



RN 7647-01-0 HCAPLUS

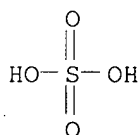
CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

*not included among inorganic acids*

HCl

RN 7664-93-9 HCAPLUS

CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



L16 ANSWER 12 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 1986:487429 HCAPLUS

DN 105:87429

TI Tantalum-niobium alloys as materials for electrolytic capacitors

AU Chamdawalla, N.; Ettmayer, P.; Leuprecht, R.; Aschenbrenner, W.;  
Bildstein, H.

CS Inst. Chem. Technol. Anorg. Stoffe, TU Wien, Vienna, Austria

SO Metall (Berlin) (1986), 40(7), 676-9

CODEN: MTLLAF; ISSN: 0026-0746

DT Journal

LA German

CC 72-7 (Electrochemistry)

Section cross-reference(s): 76

AB The properties of Ta-Nb-alloys with respect to their use in electrolytic

*etching with  
HF, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and  
1,2 ethanediol*

foil condensers were examd. by measuring the **etching** factor, the formability of Ta-Nb foils and the residual current of Ta-Nb alloy wires used for contact leads. Alloys with Nb contents <25 wt.-% can be used instead of unalloyed Ta without loss of quality. If the **etching** and forming procedures were optimized for different **compns.**, the use of alloys with <50 wt.-% Nb for capacitors might be feasible.

ST tantalum niobium alloy electrolytic capacitor; anodization tantalum niobium alloy; **etching** electrochem tantalum niobium alloy

IT Anodization  
(of niobium-tantalum alloys as materials for electrolytic capacitors)

IT **Etching**  
(electrochem., of niobium-tantalum alloys as materials for electrolytic capacitors)

IT Electric capacitors  
(electrolytic, niobium-tantalum alloys as materials for)

IT 37237-20-0  
RL: RCT (Reactant)  
(**etching** of, as material for electrolytic capacitors)

IT 7664-38-2, uses and miscellaneous  
RL: USES (Uses)  
(in anodization, of niobium-tantalum alloys as materials for electrolytic capacitors)

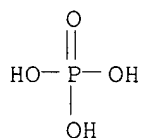
IT 67-56-1, uses and miscellaneous 107-21-1, uses and miscellaneous 10043-52-4, uses and miscellaneous 12124-97-9  
RL: USES (Uses)  
(in electrolytic **etching** of niobium-tantalum alloy foils as materials for electrolytic capacitors)

IT 7664-39-3, uses and miscellaneous 7664-93-9, uses and miscellaneous 7697-37-2, uses and miscellaneous  
RL: USES (Uses)  
(in **etching**, of niobium-tantalum wires as materials for electrolytic capacitors)

IT 7664-38-2, uses and miscellaneous  
RL: USES (Uses)  
(in anodization, of niobium-tantalum alloys as materials for electrolytic capacitors)

RN 7664-38-2 HCAPLUS

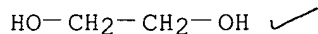
CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



IT 107-21-1, uses and miscellaneous  
RL: USES (Uses)  
(in electrolytic **etching** of niobium-tantalum alloy foils as materials for electrolytic capacitors)

RN 107-21-1 HCAPLUS

CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



IT 7664-39-3, uses and miscellaneous 7664-93-9, uses and miscellaneous 7697-37-2, uses and miscellaneous

RL: USES (Uses)

(in **etching**, of niobium-tantalum wires as materials for electrolytic capacitors)

RN 7664-39-3 HCAPLUS

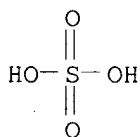
CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

HF, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>

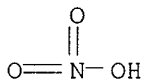
RN 7664-93-9 HCAPLUS

CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS

CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



L16 ANSWER 13 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 1980:50109 HCAPLUS

DN 92:50109

TI Removing a cured epoxy resin film from a metal surface

IN Wong, Ching-Ping

PA Western Electric Co., Inc., USA

SO U.S., 6 pp.

CODEN: USXXAM

DT Patent

LA English

IC B29C017-08

NCL 156630000

CC 74-8 (Radiation Chemistry, Photochemistry, and Photographic Processes)

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4171240	A	19791016	US 1978-900367	19780426

AB Cured epoxy resin adhesives, which are used to laminate Cu or other material to a suitable support in the prodn. of a photomask, can be removed by treatment with a swelling agent, then treatment with an oxidizing agent, and subsequently treatment with an **etchant** comprising H<sub>2</sub>SO<sub>4</sub>. Thus, a laminate consisting of a Teflon 100 FEP support, an epoxy resin adhesive layer, and a Cu layer was coated on the Cu layer with Riston 116S photoresist, stored in the dark from 0.5 to 1 h, imagewise exposed, the photoresist developed in 1,1,1-trichloroethylene, the exposed Cu layer removed by **etching**, the exposed epoxy resin swollen in CH<sub>2</sub>Cl<sub>2</sub>, immersed in 10% aq. ammonium persulfate at 25.degree. for 30 s, and then immersed in 98% H<sub>2</sub>SO<sub>4</sub> at 145° for 7 s to completely remove the exposed epoxy resin and give a finished photomask.

ST epoxy resin removal photomask manuf; adhesive epoxy removal fabrication photomask

IT Epoxy resins, uses and miscellaneous  
RL: USES (Uses)  
(adhesives, removal of, in photomask fabrication)

IT Photomasks  
(epoxy resin adhesive removal in fabrication of)

IT Adhesives  
(epoxy resins, removal of, in fabrication of photomasks)

IT 25068-38-6  
RL: USES (Uses)  
(adhesive, removal of, in photomask fabrication)

IT 103-83-3 112-24-3 121-69-7, uses and miscellaneous 25134-21-8  
RL: USES (Uses)  
(epoxy resin adhesive **compns.** contg., removal of, in fabrication of photomasks)

IT 67-56-1, uses and miscellaneous **7664-38-2**, uses and miscellaneous **7664-39-3**, uses and miscellaneous **7664-93-9**, uses and miscellaneous 7722-84-1, uses and miscellaneous 7727-54-0 11115-74-5  
RL: USES (Uses)  
(in epoxy resin adhesive removal in photomask fabrication)

IT 68-12-2, properties 75-09-2, properties 75-75-2 76-05-1, properties 78-93-3, properties 109-99-9, properties 110-86-1, uses and miscellaneous  
RL: PRP (Properties)  
(in epoxy resin adhesive removal in photomask fabrication)

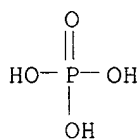
IT 71-55-6 76-13-1 123-42-2 123-91-1, properties 872-50-4, properties  
RL: USES (Uses)  
(in epoxy resin adhesive removal in photomasks fabrication)

IT **64-17-5**, properties 64-18-6, uses and miscellaneous 67-64-1, properties **107-21-1**, properties 7705-08-0, properties  
RL: PRP (Properties)  
(in epoxy resin adhesive removal in photomasks fabrication)

IT **7664-38-2**, uses and miscellaneous **7664-39-3**, uses and miscellaneous **7664-93-9**, uses and miscellaneous  
RL: USES (Uses)  
(in epoxy resin adhesive removal in photomask fabrication)

RN 7664-38-2 HCAPLUS

CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



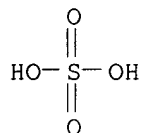
RN 7664-39-3 HCAPLUS

CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

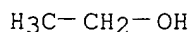
HF

RN 7664-93-9 HCAPLUS

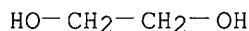
CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



IT 64-17-5, properties 107-21-1, properties  
 RL: PRP (Properties)  
 (in epoxy resin adhesive removal in photomasks fabrication)  
 RN 64-17-5 HCAPLUS  
 CN Ethanol (9CI) (CA INDEX NAME)



RN 107-21-1 HCAPLUS  
 CN 1,2-Ethanediol (9CI) (CA INDEX NAME)



L16 ANSWER 14 OF 14 HCAPLUS COPYRIGHT 2002 ACS

AN 1971:90314 HCAPLUS

DN 74:90314

TI Metallography of superalloys

AU Kohlhaas, Erich; Fischer, Alfred

CS Versuchsanst. Roehling'sche Eisen Stahlwerke G.m.b.H., Voelkingen, Ger.

SO Prakt. Metallogr. (1971), 8(1), 3-25

CODEN: PMTLA5

DT Journal

LA English/German

CC 56 (Nonferrous Metals and Alloys)

AB The complex **compn.** of 17 superalloys (high-temp. Fe-, Ni-, and Co-base alloys) and their use in a 550-1000.degree. range, sometimes for long periods, results in an extraordinary diversity of structural components. The amt. of the .gamma.'-phase pptd., its particle size, form, and configuration as well as its final transformation into other phases cause significant changes in the properties of the superalloys. For a comprehensive picture of the structures, all available light and electron microscopic methods supplemented by x-ray diffraction pictures and electron beam microprobe measurements are used. Observations are made of normal and freckle segregations. In the study of **etched** disks, **compns.** of 4 **macroetching** reagents included FeCl<sub>3</sub>, HCl, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>. The quantity, form, and distribution of nonmetallic inclusions (oxides, sulfides, silicates, coarse ppts.) are evaluated. **Compns.** of 11 chem. and electrolytic **etching** reagents for revealing structure and producing thin foils included CuSO<sub>4</sub>, HCl, HNO<sub>3</sub>, EtOH, HF, glycerol, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, HOAc, CrO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, MeOH, and lactic acid. The actual size and shape of the .gamma.'-particles can be revealed only in extn. micrographs. Metallographic preparative techniques are illustrated.

ST superalloy metallog; metallog superalloy; iron superalloy metallog; nickel superalloy metallog; cobalt superalloy metallog

IT Cobalt alloys, base

Iron alloys, base

Nickel alloys, base

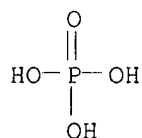
*etchant includes*  
 HCl, HNO<sub>3</sub>, HF, H<sub>2</sub>SO<sub>4</sub>, HOAc, H<sub>3</sub>PO<sub>4</sub>,  
 lactic acid, glycerol, EtOH, MeOH



(**etching** of complex, for metallography)  
 IT Alloys, reactions  
 RL: RCT (Reactant)  
 (**etching** of super-, for metallography)  
 IT **Etching**  
 (of superalloys, for metallography)  
 IT 50-21-5, reactions 64-19-7, reactions **7647-01-0**, reactions  
**7664-38-2**, reactions **7664-39-3**, reactions  
**7664-93-9**, reactions **7697-37-2**, reactions 7758-98-7,  
 reactions  
 RL: RCT (Reactant)  
 (**etching** by, of superalloys for metallography)  
 IT 56-81-5, uses and miscellaneous **64-17-5**, uses and miscellaneous  
 67-56-1, uses and miscellaneous 1333-82-0 7722-84-1, uses and  
 miscellaneous  
 RL: USES (Uses)  
 (in **etching**, of superalloys for metallography)  
 IT **7647-01-0**, reactions **7664-38-2**, reactions  
**7664-39-3**, reactions **7664-93-9**, reactions  
**7697-37-2**, reactions  
 RL: RCT (Reactant)  
 (**etching** by, of superalloys for metallography)  
 RN 7647-01-0 HCAPLUS  
 CN Hydrochloric acid (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

HCl

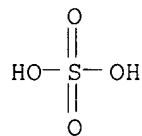
RN 7664-38-2 HCAPLUS  
 CN Phosphoric acid (7CI, 8CI, 9CI) (CA INDEX NAME)



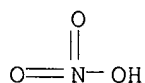
RN 7664-39-3 HCAPLUS  
 CN Hydrofluoric acid (8CI, 9CI) (CA INDEX NAME)

HF

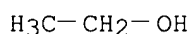
RN 7664-93-9 HCAPLUS  
 CN Sulfuric acid (8CI, 9CI) (CA INDEX NAME)



RN 7697-37-2 HCAPLUS  
 CN Nitric acid (8CI, 9CI) (CA INDEX NAME)



IT 64-17-5, uses and miscellaneous  
 RL: USES (Uses)  
 (in **etching**, of superalloys for metallography)  
 RN 64-17-5 HCAPLUS  
 CN Ethanol (9CI) (CA INDEX NAME)



*Text search*

=> D QUE

L3 24 SEA FILE=REGISTRY ABB=ON (10043-35-3/BI OR 106-69-4/BI OR 107-21-1/BI OR 107-41-5/BI OR 107-88-0/BI OR 111-29-5/BI OR 25265-71-8/BI OR 463-79-6/BI OR 50-70-4/BI OR 54289-82-6/BI OR 57-55-6/BI OR 64-17-5/BI OR 67-63-0/BI OR 71-23-8/BI OR 71-36-3/BI OR 7440-21-3/BI OR 7440-56-4/BI OR 7601-90-3/BI OR 7631-86-9/BI OR 7664-39-3/BI OR 7664-93-9/BI OR 7697-37-2/BI OR 7782-99-2/BI OR 78-83-1/BI)

L4 17 SEA FILE=REGISTRY ABB=ON L3 AND OL

L8 6 SEA FILE=REGISTRY ABB=ON SULFURIC ACID/CN OR BORIC ACID/CN OR CARBONIC ACID/CN OR PERCHLORIC ACID/CN OR SULFUROUS ACID/CN

L9 14 SEA FILE=REGISTRY ABB=ON L4 NOT (1/S OR 1/SI)

L10 5 SEA FILE=REGISTRY ABB=ON NITRIC ACID/CN OR PHOSPHORIC ACID/CN OR HYDROCHLORIC ACID/CN OR HYDROFLUORIC ACID/CN OR HYDROBROMIC ACID/CN

L11 222913 SEA FILE=HCAPLUS ABB=ON L9

L12 96226 SEA FILE=HCAPLUS ABB=ON L8

L13 151500 SEA FILE=HCAPLUS ABB=ON L10

L14 1478 SEA FILE=HCAPLUS ABB=ON L11 AND L12 AND L13

L15 105 SEA FILE=HCAPLUS ABB=ON L14 AND ?ETCH?

L16 14 SEA FILE=HCAPLUS ABB=ON L15 AND (COMPNS OR COMPOSITION?)

L18 32 SEA FILE=HCAPLUS ABB=ON (ALCOHOL# OR ALC) AND (INORG?(3A)ACID#) AND ?ETCH?

L19 6 SEA FILE=HCAPLUS ABB=ON L18 AND (COMPNS OR COMPOSITION?)

L20 37 SEA FILE=HCAPLUS ABB=ON (?GLYCOL?) AND (INORG?(3A)ACID#) AND ?ETCH?

L21 10 SEA FILE=HCAPLUS ABB=ON L20 AND (COMPNS OR COMPOSITION?)

L23 63991 SEA FILE=HCAPLUS ABB=ON (?GLYCOL? OR ALC OR ALCOHOL#) AND ((SULFURIC OR BORIC OR CARBONIC OR PERCHLORIC OR SULFUROUS) (W)A CID# OR H2SO4 OR H2SO3 OR H2CO3 OR H3BO3 OR HClO4)

L24 27061 SEA FILE=HCAPLUS ABB=ON L23 AND (HCL OR HBR OR HF OR HNO3 OR HNO2 OR H3PO4 OR H3PO3 OR (HYDROCHLORIC OR HYDROBROMIC OR HYDROFLUORIC OR NITRIC OR NITROUS OR PHOSPHORIC OR PHOSPHOROUS) (W)ACID#)

L25 851 SEA FILE=HCAPLUS ABB=ON L24 AND ?ETCH?

L26 87 SEA FILE=HCAPLUS ABB=ON L25 AND (COMPNS OR COMPOSITION?)

L27 9 SEA FILE=HCAPLUS ABB=ON L26 AND (2 OR TWO) (2W)ACID#

L28 2 SEA FILE=HCAPLUS ABB=ON 26 AND TWO(W)INORGAN?

L29 24 SEA FILE=HCAPLUS ABB=ON L19 OR L21 OR L27 OR L28

L31 13 SEA FILE=HCAPLUS ABB=ON L29 AND ETCH?

L33 16 SEA FILE=HCAPLUS ABB=ON L29 NOT STRETCH?

L34 16 SEA FILE=HCAPLUS ABB=ON L33 OR L31  
L35 15 SEA FILE=HCAPLUS ABB=ON (L34 OR L16) NOT L16

=> D L35 ALL 1-15 HITSTR

L35 ANSWER 1 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 2001:795122 HCAPLUS

DN 135:347911

TI **Etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications

IN Klein, Sylke; Heider, Lilia; Zielinski, Claudia; Kuebelbeck, Armin; Stockum, Werner

PA Merck Patent G.m.b.H., Germany

SO Ger. Offen., 8 pp.

CODEN: GWXXBX

DT Patent

LA German

IC ICM C03C015-00

ICS C04B041-91; H01L021-311; H01L031-18; H01L031-0392; H01L023-08

CC 57-4 (Ceramics)

Section cross-reference(s): 76

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10101926	A1	20011031	DE 2001-10101926	20010116
WO 2001083391	A1	20011108	WO 2001-EP3317	20010323
W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, -KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				

PRAI DE 2000-10020817 A1 20000428

DE 2001-10101926 A 20010116

AB The new **etching compns.** in the form of printable, homogeneous, particle-free corroding pastes with non-Newtonian flow behavior are developed for corroding glassy and cryst. surfaces of glazes, preferably on SiO<sub>2</sub>- and Si<sub>3</sub>N<sub>4</sub>-based glazes and their layers. The pastes contain (a) .gtoreq.1 **etching** component esp. NH<sub>4</sub>HF<sub>2</sub>, (b) a solvent (e.g., propylene carbonate), (c) a thickener (e.g., ethylcellulose), (d) org. and/or **inorg. acid** such as formic acid or lactic acid, and (e) a foaming agent, a thixotropic agent, e.g., triethylene **glycol** monomethyl ether or ethylene **glycol** monobutyl ether, an adhesive such as PVP K-120 or PVP K-90, and a plasticizer.

ST silica glaze **etching** paste semiconductor photovoltaic

IT Plasticizers

(**etching** paste component; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)

IT **Etching**

(**etching** paste; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)

IT Glazes (vitreous)

(glassy and cryst. surfaces of; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry

applications)  
 IT Photoelectric devices  
 Semiconductor materials  
 (glazes; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 9003-39-8, PVP K-120  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (PVP K-120 and PVP K-90, adhesives; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 1341-49-7, Ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>)  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (**etching** component; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 50-21-5, Lactic acid, uses 64-18-6, Formic acid, uses  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (**etching** paste component; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 7631-86-9, Silica, uses 12033-89-5, Silicon nitride, uses  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (glaze based on; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 108-32-7, Propylene carbonate  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (solvent; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 9004-57-3, Ethylcellulose  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (thickener; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)  
 IT 111-76-2, Ethylene glycol monobutyl ether 112-35-6, Triethylene glycol monomethyl ether  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (thixotropic agent; **etching** pastes for glaze surfaces for semiconductor, photovoltaic, and glass industry applications)

X L35 ANSWER 2 OF 15 HCAPLUS COPYRIGHT 2002 ACS  
 AN 2001:649874 HCAPLUS  
 DN 135:187835  
 TI Cleaning and **etching compositions** for silicon and silicon oxide compound substrates for display devices  
 IN Lee, Ki Won  
 PA S. Korea  
 SO U.S., 18 pp., Cont.-in-part of U.S. 6,194,365.  
 CODEN: USXXAM  
 DT Patent  
 LA English  
 IC ICM C03C025-68  
 NCL 510175000  
 CC 74-13 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)  
 FAN.CNT 2

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 6284721	B1	20010904	US 1999-358111	19990721
US 6194365	B1	20010227	US 1998-142750	19980915
PRAI KR 1997-1539	A	19970121		
KR 1997-53384	A	19971017		

US 1998-142750 A2 19980915  
WO 1998-KR11 W 19980121

AB A cleaning and **etching compn.** for cleaning and **etching** substrates comprising quartz, glass, Si oxide or Si as a main constituent is disclosed. A cleaning **compn.** for cleaning substrates having a Si oxide layer comprises: a fluoride which decomps. and releases F<sup>-</sup> ion in aq. soln. during cleaning and **etching** processes for reacting with Si; and a persulfate which decomps. and releases H<sub>2</sub>O<sub>2</sub> in the aq. soln. for increasing the oxidn. effect of the fluoride. Display device substrates having Si oxide layer and LCD glass substrates can be cleaned without imparting damages, as a result, a safe cleaning process can be implemented. A cleaning **compn.** for cleaning substrates having a Si layer comprises a fluoride, an **inorg. acid and/or HNO<sub>3</sub>**. The above cleaning **compns.** can also be suitably used as an **etchant** for **etching** Si and Si oxide layers. The cleaning and **etching compn.** of the present invention provides an effective control of **etching** rates, thus the factors related to the **etching** process can be flexibly adjusted.

ST cleaning **etching** silicon oxide display substrate  
IT Cleaning

**Etching**

Glass substrates  
Liquid crystal displays  
Optical imaging devices  
Oxidation  
Process control

(cleaning and **etching compns.** for silicon and silicon compd. substrates for display devices)

IT Fluorides, processes  
Nitrates, processes

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(cleaning and **etching compns.** for silicon and silicon compd. substrates for display devices)

IT Silicate glasses

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)

(cleaning and **etching compns.** for silicon and silicon compd. substrates for display devices)

IT **Acids, processes**

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(**inorg.**; cleaning and **etching compns.** for silicon and silicon compd. substrates for display devices)

IT Aluminum alloy, base

RL: PEP (Physical, engineering or chemical process); TEM (Technical or engineered material use); PROC (Process); USES (Uses)

(cleaning and **etching compns.** for silicon and silicon compd. substrates for display devices)

IT 64-19-7, Acetic acid, processes 67-63-0, Isopropyl alcohol,

processes 1306-38-3, Cerium dioxide, processes 1333-83-1, Sodium bifluoride 1341-49-7, Ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) 3006-15-3, Sodium dihexyl sulfosuccinate 5329-14-6, Sulfamic acid 6484-52-2, Nitric acid ammonium salt, processes 7631-99-4, Nitric acid sodium salt, processes 7647-01-0, Hydrochloric acid, processes 7664-38-2, Phosphoric acid, processes 7664-39-3, Hydrofluoric acid, processes 7681-49-4, Sodium fluoride, processes 7697-37-2, Nitric acid, processes 7727-21-1, Potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) 7727-54-0, Ammonium persulfate 7757-79-1, Potassium nitrate, processes 7775-27-1, Sodium persulfate

Contains  
acetic acid  
(organic  
acid)

7787-32-8, Barium fluoride 7789-23-3, Potassium fluoride (KF)  
7789-29-9, Potassium bifluoride 10022-31-8, Barium nitrate 12135-76-1,  
Ammonium sulfide ((NH<sub>4</sub>)<sub>2</sub>S) 13826-83-0, Ammonium tetrafluoroborate  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical  
process); PROC (Process); USES (Uses)

(cleaning and **etching compns.** for silicon and  
silicon compd. substrates for display devices)

IT 7722-84-1P, Hydrogen peroxide, reactions  
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical  
process); PNU (Preparation, unclassified); RCT (Reactant); PREP  
(Preparation); PROC (Process); RACT (Reactant or reagent); USES (Uses)

(cleaning and **etching compns.** for silicon and  
silicon compd. substrates for display devices)

IT 7440-21-3, Silicon, processes 7631-86-9, Silicon dioxide, processes  
12033-89-5, Silicon nitride, processes 39396-75-3  
RL: PEP (Physical, engineering or chemical process); TEM (Technical or  
engineered material use); PROC (Process); USES (Uses)

(cleaning and **etching compns.** for silicon and  
silicon compd. substrates for display devices)

IT 15092-81-6, Peroxydisulfate ((SO<sub>3</sub>)<sub>2</sub>O<sub>2</sub>) 16984-48-8, Fluoride, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)

(cleaning and **etching compns.** for silicon and  
silicon compd. substrates for display devices)

RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD  
RE

- (1) Anon; AT 183883 1955
- (2) Anon; DE 1209844 1966 HCAPLUS
- (3) Anon; GB 1276550 1972 HCAPLUS *includes H<sub>2</sub>O*
- (4) Anon; EP 0106301 A1 1984 HCAPLUS
- (5) Barcelona; US 5164018 1992 HCAPLUS *contains H<sub>2</sub>O*
- (6) Carlson; US 5393447 1995 HCAPLUS *-contains H<sub>2</sub>O*
- (7) Hopkins; US 4517106 1985 HCAPLUS *HF and alcohol*
- (8) Ikeda; US 5688755 1997 HCAPLUS *one mineral acid and C<sub>2</sub>-C<sub>10</sub> glycol*
- (9) Kendall; US 3725224 1973 HCAPLUS *H<sub>2</sub>SO<sub>4</sub>, HAc and alcohol*
- (10) Loch; US 4614607 1986 HCAPLUS ~~X~~
- (11) Mann; US 3654001 1972 HCAPLUS ~~X~~ *aqueous soln*
- (12) Murphy; US 5810938 1998 HCAPLUS ~~X~~
- (13) Radimer; US 3565707 1971 HCAPLUS ~~X~~
- ~~X~~(14) Salzle; US 4555304 1985 HCAPLUS *H<sub>2</sub>SO<sub>4</sub> + HF X, lacks alcohol*
- (15) Shiga; US 3986970 1976 HCAPLUS ~~X~~ *aqueous soln*
- (16) Yee; US 5211807 1993 HCAPLUS ~~X~~ *HF and HNO<sub>3</sub>*

L35 ANSWER 3 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1992:429647 HCAPLUS

DN 117:29647

TI Measurement of diffusivity in molybdenum oxide (MoO<sub>3</sub>)-manganese molybdenum  
oxide (MnMoO<sub>4</sub>) system

AU Murthy, J. S. N.; Satyanarayana, M.

CS Coll. Technol., Osmania Univ., Hyderabad, India

SO J. Inst. Eng. (India), Chem. Eng. Div. (1990), 71(2), 44-7

CODEN: JECEAF; ISSN: 0020-3351

DT Journal

LA English

CC 48-8 (Unit Operations and Processes)

AB Diffusivity measurements between **two inorg. solids**,  
namely, molybdenum trioxide (MoO<sub>3</sub>) and manganese molybdate (MnMoO<sub>4</sub>) were  
undertaken with compaction pressure (porosity) and diffusion temp. as  
variables. The exptl. technique of measurement and establishment of  
concn. profile by electron probe micro analyzer (EPMA) for the diffusion  
of Mo<sup>6+</sup> ions into manganese molybdate from which diffusivities are detd

*Different  
field of  
endeavor*

are described. The activation energy required for the diffusion is calcd. and reported for three porosities of manganese molybdate, namely, 10.56 kcal/g-mol, 16.14 kcal/g-mol and 19.37 kcal/g-mol for compaction pressures 2040 N/cm<sup>2</sup> (percentage .epsilon.0 of MnMoO<sub>4</sub> = 33.4), 4510 N/cm<sup>2</sup> (percentage .epsilon.0 = 26.13) and 9910 N/cm<sup>2</sup> (.epsilon.0 = 23.16), resp. A generalized correlation is presented for diffusivity in terms of diffusion temp. and porosity of manganese molybdate.

ST diffusivity molybdenum oxide manganese molybdenum oxide

IT Diffusion

(of molybdenum ions into manganese molybdate, measurement of)

IT 16065-87-5, Molybdenum ion(6+), properties

RL: PEP (Physical, engineering or chemical process); PROC (Process)

(diffusion of, into manganese molybdate, measurement of)

IT 14013-15-1, Manganese molybdate

RL: USES (Uses)

(molybdenum ion diffusion into, measurement of)

L35 ANSWER 4 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1991:57646 HCAPLUS

DN 114:57646

TI Reconstitution of the phosphoglycerate transport protein of Salmonella typhimurium

AU Varadhachary, Atul; Maloney, Peter C.

CS Dep. Physiol., Johns Hopkins Sch. Med., Baltimore, MD, 21205, USA

SO J. Biol. Chem. (1991), 266(1), 130-5

CODEN: JBCHA3; ISSN: 0021-9258

DT Journal

LA English

CC 6-1 (General Biochemistry)

AB Operation of the phosphoglycerate transport protein (PgtP) of S. typhimurium has been studied in proteoliposomes by using a technique in which membrane protein is solubilized and reconstituted directly from small vols. of cell cultures. When protein from induced cells was reconstituted into phosphate (Pi)-loaded proteoliposomes, it was possible to demonstrate a PgtP-mediated exchange of internal and external phosphate. For this homologous Pi:Pi antiport, kinetic anal. indicated a Michaelis const. (Kt) of 1 mM and a maximal velocity of 26 nmol/min mg of protein; arsenate inhibited with a Ki of 1.3 mM, suggesting that PgtP did not discriminate between these **two inorg** . substrates. Pi-loaded proteoliposomes also accumulated 3-phosphoglycerate and phosphoenolpyruvate, establishing for each of them a concn. gradient (in/out) of .apprx.100-fold; phosphoenolpyruvate (Ki = 70 .mu.M) rather than 3-phosphoglycerate (Kt = 700, Ki = 900 .mu.M) was the preferred substrate for these conditions. Thus, such heterologous exchange was a neutral event, since its rate and extent were unaffected by the presence of a protonophore and unresponsive to the imposition of a membrane potential (pos. or neg. inside). In quant. work, a stoichiometry of 1:1 for the exchange of Pi and 3-phosphoglycerate was detd. Given an electroneutral exchange, this finding is most easily understood as the overall exchange of divalent Pi against divalent phosphoglycerate. These expts. establish that PgtP functions as an anion exchange protein and that it shares important mechanistic features with the Pi-linked antiporters, GlpT and UhpT, responsible for transport of glycerol 3-phosphate and hexose 6-phosphates into Escherichia coli.

ST phosphoglycerate transport protein Salmonella

IT Salmonella typhimurium

(phosphoglycerate-transporting protein of, phosphoglycerate and phosphate electroneutral antiport by)

IT Biological transport

(antiport, electroneutral, of phosphoglycerate and phosphate, by

phosphoglycerate-transporting protein reconstituted form, of Salmonella typhimurium)

IT Proteins, specific or class  
RL: BIOL (Biological study)  
(phosphoglycerate-transporting, phosphoglycerate and phosphate electroneutral antiporting by reconstituted form of, of Salmonella typhimurium)

IT 820-11-1, Phosphoglyceric acid  
RL: BIOL (Biological study)  
(antiport of, with divalent phosphate by phosphoglycerate-transporting protein reconstituted form, of Salmonella tryphimurium)

IT 14265-44-2, Phosphate, biological studies  
RL: BIOL (Biological study)  
(antiport of, with phosphoglycerate by phosphoglycerate-transporting protein reconstituted form, of Salmonella tryphimurium)

L35 ANSWER 5 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1985:212734 HCAPLUS

DN 102:212734

TI Aluminum surface preparation

IN Walls, John E.

PA American Hoechst Corp., USA

SO U.S., 6 pp.

CODEN: USXXAM

DT Patent

LA English

IC ICM C25F003-04

ICS C25D011-16; C25D011-18

NCL 204033000

CC 74-6 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

Section cross-reference(s): 72

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4502925	A	19850305	US 1984-619105	19840611
	EP 167751	A1	19860115	EP 1985-105850	19850513
	EP 167751	B1	19900718		
	R: CH, DE, FR, GB, LI, NL, SE				
	AU 8542806	A1	19851219	AU 1985-42806	19850523
	AU 584899	B2	19890608		
	CA 1235380	A1	19880419	CA 1985-482400	19850527
	BR 8502751	A	19860212	BR 1985-2751	19850610
	JP 61010491	A2	19860117	JP 1985-125265	19850611
PRAI	US 1984-619105		19840611		

AB A prepn. is described of an Al support for lithog. printing plates fabrication. The support having an increased surface area and improved capillary wettability is prepd. by **etching** in an aq. bath contg. **HNO3** and/or **HCl** .ltoreq.25 and an **inorg.** F-contg. **acid** or a salt 1-25%, electrochem. grained and anodized. Thus, a 1100 Al alloy degreased in an alk. soln. was immersed in a **compn.** contg. (100%) **HNO3** 100, **NH4F** 100 g/L for 60 s at 60.degree., rinsed, dried to provide a highly textured surface contg. uniformly distributed nodules 10.mu. in diam., 8-10.mu. in height and 40-50.mu. from peak-to-peak. The support was then anodized using d.c. electricity and an electrolyte contg. 150 g/L of H2SO4, hydrophilized by treating with a 2.2 g/L soln. of poly(vinylphosphonic acid) at 65.5.degree. for 30 s, rinsed, dried, coated with a photosensitive **compn.** contg. poly(vinyl formal-vinyl **alc.**-vinyl acetate), **H3PO4**, phthalocyanine, and a condensation product of 3-methoxy-4-diazodiphenylamine sulfate and 4,4'-



bismethoxymethyldiphenyl ether, imagewise exposed and developed. The obtained printing provided 50,000 acceptable copies.

ST aluminum support **etching** lithog plate

IT Lithographic plates

(aluminum surface prepn. for support for, **etching** in, in aq. soln. contg. nitric acid and/or hydrochloric acid and **inorg.** fluorine-contg. acid or salt)

IT Sulfonic acids, uses and miscellaneous

RL: USES (Uses)

(electrochem. graining electrolyte contg., in treatment of aluminum support for lithog.)

IT 144-62-7, uses and miscellaneous 7446-70-0, uses and miscellaneous

7722-84-1, uses and miscellaneous 7727-21-1 7727-54-0 7775-27-1

10043-35-3, uses and miscellaneous 13473-90-0 15092-81-6 18697-38-6

RL: USES (Uses)

(electrochem. graining electrolyte contg., in treatment of aluminum support for lithog.)

IT 7647-01-0, uses and miscellaneous 7697-37-2, uses and miscellaneous

RL: USES (Uses)

(**etching** soln. contg. **inorg.** fluorine-contg. acid and, for surface prepn. of aluminum plate, for lithog.)

IT 1341-49-7 7664-39-3, uses and miscellaneous 12125-01-8 16872-11-0

16919-27-0 16923-95-8 16940-81-1 16961-83-4

RL: USES (Uses)

(**etching** soln. contg. nitric and/or hydrochloric acid and, for surface prepn. of aluminum plate, for lithog.)

IT 7429-90-5, uses and miscellaneous

RL: USES (Uses)

(support for lithog. printing plates from, **etching** solns. for prepn. of surface of)

*lack  
non-aqueous  
medium*

L35 ANSWER 6 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1984:597110 HCAPLUS

DN 101:197110

TI Film-removing and **etching** agent

IN Dodge, Paul D.

PA Tennant Co., USA

SO Ger. Offen., 22 pp.

CODEN: GWXXBX

DT Patent

LA German

IC C09K013-06; C04B041-32

CC 58-2 (Cement, Concrete, and Related Building Materials)

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 3401570	A1	19840719	DE 1984-3401570	19840118
	US 4469525	A	19840904	US 1983-459238	19830119
	NL 8400134	A	19840816	NL 1984-134	19840116
	GB 2136825	A1	19840926	GB 1984-1126	19840117
	GB 2136825	B2	19861119		
	US 4608086	A	19860826	US 1984-644856	19840827
PRAI	US 1983-459238		19830119		

AB Combined film removers and **etching** agents for concrete for removal of temporary curing films and surface prepn. for permanent protective coatings are prepd. from an org. solvent 1-10, solvent distributor 30-50, an acid-resistant surfactant 1-5, a weak org. acid 5-20, a strong inorg. or org. acid 20-30, and water <30 wt. parts. Thus, HCl 25, glycolic acid [79-14-1] 25, dipropylene glycol Me ether [12002-25-4] 10, 2-butoxyethanol

*X  
uses  
H<sub>2</sub>O*

[111-76-2] 15, a nonionic surfactant 5, and CH<sub>2</sub>Cl<sub>2</sub> [75-09-2] 15 parts were combined to give a storage-stable nonaq. soln. This soln. was combined with 100 parts arom. solvent with Kurl-butanol test value 92 and applied as a layer .apprx.0.4 mm thick to remove a thin chlororubber film from a concrete plate. The acid system was activated by applying 100 parts water. After 10-15 min the acid was removed by a wet suction roller and the concrete surface was rinsed with water until it had a pH of .apprx.8. The degree of film removal and **etching** were satisfactory.

ST film remover **etchant** concrete

IT Concrete

(curing film removal from and **etching** of, **comps.** for)

IT Rubber, chlorinated

RL: USES (Uses)

(curing films, on concrete, **comps.** for removal of, and concrete **etching**)

IT Coating removers

(for curing films, on concrete and for **etching**)

IT Petroleum spirits

Petroleum spirits

RL: TEM (Technical or engineered material use); USES (Uses)

(in curing film removers and **etching comps.** for concrete)

IT **Etching**

(of concrete, agents for curing film removal and)

IT 92909-16-5 92909-22-3

RL: USES (Uses)

(curing films, on concrete, **comps.** for removal of, and concrete **etching**)

IT 64-18-6, uses and miscellaneous 64-19-7, uses and miscellaneous  
67-56-1, uses and miscellaneous 67-63-0, uses and miscellaneous  
75-09-2, uses and miscellaneous 75-21-8, uses and miscellaneous  
77-92-9, uses and miscellaneous 78-83-1, reactions 78-87-5 79-14-1,  
uses and miscellaneous 110-49-6 110-80-5 111-15-9 111-76-2  
111-96-6 127-18-4, uses and miscellaneous 1336-21-6 5329-14-6  
7382-32-3 7647-01-0, uses and miscellaneous 7664-38-2, uses and  
miscellaneous 7664-39-3, uses and miscellaneous 9016-45-9 12002-25-4  
26264-05-1 92909-18-7

RL: TEM (Technical or engineered material use); USES (Uses)

(in curing film removers and **etching comps.** for concrete)

L35 ANSWER 7 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1979:11098 HCAPLUS

DN 90:11098

TI Metal cleaning and polishing solutions

IN Shiga, Shoji; Inada, Takashi

PA Furukawa Electric Co., Ltd., Japan; Furukawa Kinzoku Kogyo K. K.

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC C23F001-00

CC 56-5 (Nonferrous Metals and Alloys)

Section cross-reference(s): 46

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 53081439	A2	19780718	JP 1976-153322	19761222

X  
uses  
H<sub>2</sub>SO<sub>4</sub>  
peroxide  
and  
phosphate

lack alcohol

JP 54028382 B4 19790917  
 AB A polyoxyalkylane phosphate is added (0.01-100 g/L) to a soln. of **inorg. acid** and H2O2 to prep. metal cleaning, polishing, or **etching** solns. Thus, brass (35% Zn) was treated with a soln. of H2SO4, H2O2, and [R(OC2H4)nO]3PO (R = C10-16 alkyl).  
 ST metal polishing **compn**; polyethylene **glycol** phosphate  
 IT Polishing  
 (of metals, acid-hydrogen peroxide-polyoxyalkylane phosphate solns. for)  
 IT 12597-71-6, uses and miscellaneous  
 RL: USES (Uses)  
 (polishing of, with acid-peroxide soln. contg. polyethylene **glycol** phosphate)  
 IT 7664-93-9, uses and miscellaneous 7722-84-1, uses and miscellaneous  
 64502-13-2D, alkyl ethers  
 RL: USES (Uses)  
 (polishing soln. contg., for brass)

X L35 ANSWER 8 OF 15 HCAPLUS COPYRIGHT 2002 ACS  
 AN 1969:40278 HCAPLUS  
 DN 70:40278  
 TI Alkaline solutions for rapid **etching** of aluminum without hard scale formation in containers  
 IN Barber, Alan L.; Clarke, John  
 PA Bowmans Chemicals Ltd.; Forestal Industries(U.K.)Ltd.  
 SO Brit., 4 pp.  
 CODEN: BRXXAA  
 DT Patent  
 LA English  
 IC B44C  
 CC 56 (Nonferrous Metals and Alloys)  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 1134716		19681127	GB	19660226
AB	<p>Superior alk. solns. for chem. milling or selective <b>etching</b> of Al, Mg, Zn, Pb, or other metals similarly sol. in alkalis, or for the removal of such metals from other metallic surfaces, are prepd. by dissolving in H2O a solute mixt. consisting of at least 60% alkali on a dry basis, with 1-20% each of an <b>inorg.</b> salt accelerator or <b>acid</b> forming such a salt, preferably NaNO3, and a satd. aliphatic B polyhydroxy compd. scale inhibitor obtainable by treating H3BO3 or a borate with a suitable aliphatic compd. having 2 hydroxy groups on adjacent C atoms. Probable formulas are given for 3 classes of suitable N polyhydroxy compds. which include heptonic, gluconic, and lactic acids, mannitol, sorbitol, and ethylene <b>glycol</b>. A preferred mixt. is NaOH 83, NaNO3 9, and Na boroheptonate 8% by wt., the latter component being the Na salt of the acid complex (I). Solns. used for <b>etching</b> by any method usually contain 1-20% of such a mixt. by wt. and are heated to 170-212.degree.F. The rates of soln. of Al sheet specimens 0.1 in. thick weighing .apprx.1.1 g. each in various solns. at 170.degree.F. were measured after dropping each 1 of 5 pieces consecutively in the same 100-ml. batch of soln., then filtering the soln., and measuring the soln. rate of another specimen in it. A preferred <b>compn</b>. contg. <u>NaOH 82.7</u>, <u>NaNO3 9.3</u>, and Na boroheptonate 8.27 g./l. dissolved the 1st 1.1-g. specimen in 100 ml. in 50, the 2nd in 51, the 3rd in 53, the 4th in 61 min., and with full Al2O3 pptn. and no further visible reaction, 4.9 g. Al total; after filtering, an addnl. 0.5 g. of Al was dissolved in 50 min. Hard scale formation was</p>				

inhibited and any scale formed could be removed without chipping. When the soln. contained no scale inhibitor these time periods were 55, 57, 80, 100, and 56 min., resp.; and when NaNO<sub>3</sub> was also omitted they were 75, 78, 90, 120, and 80 min., resp. Pptn. of Al<sub>2</sub>O<sub>3</sub> did not begin in the preferred soln. until 1.8 g. Al had been dissolved, but it began when 1-1.3 g. had been dissolved in the others.

ST aluminum alk **etching**; alk **etching** Al; **etching**  
Al alk

IT 7429-90-5, reactions

RL: RCT (Reactant)

(**etching** of, solns. contg. sodium boroheptonate for)

IT 7631-99-4, reactions 14906-97-9 21097-80-3

RL: RCT (Reactant)

(**etching** with solns. contg. sodium hydroxide and, of aluminum)

IT 1310-73-2, reactions

RL: RCT (Reactant)

(**etching** with solns. contg., of aluminum)

X L35 ANSWER 9 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1962:24781 HCAPLUS

DN 56:24781

OREF 56:4628h-i,4629a-i,4630a-b

TI Small-ring compounds. XXXV. Studies of rearrangements in the

**nitrous acid** deaminations of methyl-substituted cyclobutyl-, cyclopropylcarbinyl-, and allylcarbinylamines

AU Silver, Marc S.; Caserio, Marjorie C.; Rice, Howard E.; Roberts, John D.

CS Massachusetts Inst. of Technol., Cambridge

SO J. Am. Chem. Soc. (1961), 83, 3671-8

DT Journal

LA Unavailable

CC 28 (Alicyclic Compounds)

AB cf. preceding abstr. -The **compns.** of the **alc.** mixts.

formed in the **HNO<sub>2</sub>**-deaminations of cyclopropylmethylcarbinylamine (I), (2-methylcyclopropyl)carbinylamine (II), 2-methylcyclobutylamine (III), 3-methylcyclobutylamine (IV), MeCH:CHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (V), and CH<sub>2</sub>:CHCH<sub>2</sub>CHMeNH<sub>2</sub> (VI) have been detd. These results and the behavior of the corresponding alcs. under isomerization conditions in strongly acidic media may be explained by assuming formation of 3 nonequiv., unsym., nonclassical cationic intermediates analogous to those previously proposed for the carbonium ion reactions of other small-ring derivs. Cyclopropyl methyl ketone (62.7 g.) reduced with 11.4 g. LiAlH<sub>4</sub> in Et<sub>2</sub>O yielded 71% cyclopropylmethylcarbinol (VII), b. 122-4.degree., n<sub>25D</sub> 1.4292-1.4298; p-nitrobenzoate m. 54-5.5.degree. (hexane). Me cyclopropyl ketoxime (20.8 g.) reduced with 11.4 g. LiAlH<sub>4</sub> in Et<sub>2</sub>O yielded 54% I; benzamide deriv. m. 96.8-7.6.degree. (hexane-C<sub>6</sub>H<sub>6</sub>). Cyclobutanone reduced with LiAlH<sub>4</sub> in Et<sub>2</sub>O yielded 80% cyclobutanol, b. 119-20 n<sub>25D</sub> 1.4333-1.4340; p-nitrobenzoate m. 84.0 5.3.degree. (hexane). 3-Methylenecyclobutanecarboxylic acid (101.5 g.), 92.5 g. Et<sub>3</sub>N, excess NH<sub>3</sub>, and 100 g. ClCO<sub>2</sub>Et in 3 l. CHCl<sub>3</sub> yielded 81% 3-methylenecyclobutanecarboxamide (VIII) m. 156.7-7.2 (sublimed). VIII in AcOH hydrogenated over prerduced PrO<sub>2</sub> gave 92% mixed cistrans-3-methylcyclobutanecarboxamide (IX), m. 154.563.0.degree. (sublimed). IX (25 g.) and MeMgI from 21.4 g. Mg and 128 g. MeI yielded 16.7 g. 3-methyl-1-acetylcyclobutane (X), b. 140-40.5.degree., n<sub>25D</sub> 1.4261; 2,4-dinitrophenylhydrazon m. 143.0-6.6.degree. (EtOH). X (11.2 g.) oxidized with 4.1 cc. 90% H<sub>2</sub>O<sub>2</sub> and 25.4 cc. (CF<sub>3</sub>CO)<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> in the presence of anhyd. Na<sub>2</sub>HPO<sub>4</sub> yielded 79% 3-methyl-1-acetoxycyclobutane (XI), b. 104.5.degree., n<sub>22.5D</sub> 1.4172. XI sapond. with alkali yielded 75% 3-methyleyclobutanol (XII), b. 133-4.degree., n<sub>25D</sub> 1.4287-4292; p-nitrobenzoate m. 50.8-69.5.degree. (hexane). 3-

Methylcyclobutanecarboxylic acid (27 g.), 50 cc. concd. **H2SO4**, 200 cc. **CHCl3**, and 19 g. **NaN3** yielded 9.2 g. IV, b. 94-5.degree., n25D 1.4290-1.4293. 2-Methyl-1,1-cyclobutanedicarboxylic acid (20-40 g.), m. 161.72.8.degree., distd. at atm. pressure gave 92-9% 2-methylcyclobutanecarboxylic acid (XIII) n25D 1.4380; amide (XIV) m. 130-3.degree.. XIV was converted with **MeMgI** to 57% mixt. of cis- and trans-1-acetyl-2-methylcyclobutane, b. 140-5.degree., b. 139.5.degree., n25D 1.4170. Crude XIVA sapond. with aq. alkali yielded 80% 2-methylcyclobutanol (XV), b. 131.degree., n25D 1.4308; p-nitrobenzoate m. 50.3-2.5.degree. (hexane). XIII was converted with **H2SO4**, **CHCl3** and **NaN3** to III, m. 92, n25D 1.4341. **CH2: CMeCH2Cl** (380 g.) treated 8 hrs. with a slow stream of O and a rapid stream of dry **HBr** gave 402 g. **BrCH2CHMeCH2Cl** (XVI), b26-28 55-63.degree., n26.5D 1.4800. **NaCN** (32.5 g.) and 88.5 g. XVI in 260 cc. 75% aq. **EtOH** refluxed 7.5 hrs., dild. to 1 l., and extd. with **CHCl3** yielded 39.6 g. **NCCH2CHMeCH2Cl** (XVII), b11.7 74-9.degree., n23D 1.4430. XVII (39 g.) and 46 g. ground **NaOH** heated 1.5 hrs. at 150-60, treated during 20 min. with 150 cc. **H2O**, heated 3 hrs., cooled to 0.degree., poured onto 100 g. ice and 37 cc. **H2SO4**, and extd. with **Et2O** yielded 23.1 g. 2-methylcyclopropanecarboxylic acid (XVIII), b17.6 97-8.degree., n21.5D 1.4384-1.4387. XVIII (23.1 g.) reduced with 7.2 g. **LiAlH4** yielded 78% 2-methylcyclopropylcarbinol (XIX) b. 133.degree., n25D 1.4283; p-nitrobenzoate, oily at room temp. **NaNH2** from 6 g. Na and 500 cc. **NH3** treated with stirring during 1 min. with 28.8 g. XVII in 50 cc. **Et2O**, dild. with 190 cc. **Et2O** during 1.5 hr., treated with 4 g. **NH4Cl**, evapd. overnight, and filtered, the filter cake dissolved in **H2O** and extd. with **Et2O**, and the combined **Et2O** solns. worked up gave 9.3 g. (2-methylcyclopropyl)carbonitrile (XX), b. 143-6.degree., n25D 1.4242. A mixt. of **ClCH2CH: CHMe** and **MeCHClCH:CH2** treated with **CuCN**, yielded **NCCH2CH:CHMe** (XXI), b. 142-4.degree., n25D 1.4199. XXI hydrolyzed and then reduced with **LiAlH4** yielded 63% **MeCH:CHCH2CH2OH** (XXII), b. 134-4.5.degree., n25D 1.4339-1.4340. XXI reduced with **LiAlH4** gave V, b. 104.5-6.5.degree., n25D 1.4345-1.4350. **MeCH:CHCHO** with **MeMgI** gave **MeCH:CHCH(OH)Me** (XXIII), b. 117-22.degree., n25D 1.4270. **AcH** treated with **Zn** and **CH2:CHCH2Br** yielded **CH2:CHCH2CH(OH)Me** (XXIV), b. 113.5-14.5.degree., n25D 1.4227. **CH2:CHCHO** with **EtMgBr** yielded **EtCH(OH)CH:CH2** (XXV), b. 112-147.degree., n25D 1.4221.1.4227. **NaN3** (15.5 g.) and 33 g. p-toluenesulfonate of XXIV in 200 cc. **MeOH** and 40 cc. **H2O** refluxed 22.5 hrs., cooled, and dild. with 200 cc. **Et2O** and 125 cc. **H2O**, the mixt. treated with 200 g. **CaCl2** in 500 cc. **H2O**, the aq. phase extd. with **Et2O**, the combined **Et2O** solns. dried and treated with 5.5 g. **LiAlH4** in **Et2O**, and the mixt. acidified, washed with **Et2O**, basified, and extd. with **Et2O** gave 2.8 g. VI; phenylthiourea deriv., m. 82.8-4.0.degree. (aq. **EtOH**). VI hydrogenated gave **MePrCHNH2**; phenylthiourea deriv, m. 73.5-4.0.degree. (aq. **EtOH**); p-nitrobenzamide m. 92.6-3.8.degree. (**C6H6**-hexane). The appropriate amine (1-10 i g.) and 22-43 g. **NaNO2** in 280 cc. **H2O** treated with stirring and cooling with 17 cc. 60% **HClO4**, distd. after about 30 rain. to collect 75 cc. homogeneous distillate, the distillate satd. with **K2CO3**, and the org. layer sepd. and analyzed showed the formation of 69% and 56% VII from I and III, resp. IV in 2 parallel runs deaminated in the usual manner gave 49 (70)% mixt. of 48 (45)% VII, 39 (39)% XXIV, 5 (6)% XII, and 8 (10)% XIX. II deaminated in the usual manner yielded 58% mixt. of 51% VII, 35% XXIV, and 13% XIX. V gave similarly 44% mixt. of 74% VII, 10% XXII, and 16% XXIII. VI (0.8 g.) deaminated in the usual manner gave 21% mixt. of 17% VII, 3% XIX, 49% XXIV, 25% XXV, and 6% **EtCH:CHCH2OH**. XV, VII, XXIV, XIX, XII, and XXII were treated with 45% **HBFe** at room temp.; XIX and VII rearranged to XXII and variable amts. of unidentified materials; the other ales. were stable. XII with 22% **HBFe** refluxed 0.5 hr. gave about 80% unchanged XII and 20% XXII; XV was completely rearranged to XXII under the same

conditions. XXII refluxed 1 hr. with 25% H<sub>2</sub>SO<sub>4</sub> gave only polymer and unrearranged XXII.

L35 ANSWER 10 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1955:64835 HCAPLUS

DN 49:64835

OREF 49:12462f-i,12463a-i,12464a-f

TI Utilization of n-alkyl methyl ketones in the Pfitzinger reaction

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CS Univ. of Texas, Austin

SO J. Am. Chem. Soc. (1954), 76, 4580-4

DT Journal

LA Unavailable

CC 10 (Organic Chemistry)

AB A series of Pfitzinger condensations [cf. Pfitzinger, J. prakt. chem. [2], 56, 283(1897)] using n-alkyl Me ketones (alkyl = Me through C<sub>6</sub>H<sub>13</sub>) has been carried out. The unsym. ketones produced 2 isomeric cinchoninic acids (I), a 2-monosubstituted

acid and a 2,3-disubstituted acid, the monosubstituted compd. usually being formed in the larger amt. A new sequence of syntheses has been developed in order to establish the structure of 1 series of these isomeric I. Isatin (II) (60 g.), 200 cc. 34% KOH in dil. EtOH, 88 g. EtAc, and 375 cc. H<sub>2</sub>O refluxed 72 hrs. with stirring, about 125 cc. liquid distd. off, the residue made faintly acidic and filtered, the filtrate acidified strongly, and the ppt. filtered off, washed, and dried gave 70 g. cryst. mixt. of isomeric I, decomp. above 300.degree. after sintering at 248.degree., which repeatedly recrystd. from H<sub>2</sub>O and aq. EtOH gave 2,3-dimethylcinchoninic acid

(III), m. above 320.degree. with rapid decompn. AcCO<sub>2</sub>H (25 g.) and 17 g. EtCHO in 100 cc. EtOH treated during 1.5 hrs. at about 5.degree. with 27 g. PhNH<sub>2</sub> in 50 cc. EtOH, the mixt. warmed gently 3 hrs., refluxed 7 hrs., concd. to 110.degree., and cooled, and the yellow solid deposit purified with EtOH and Me<sub>2</sub>CO gave 4.5 g. 2-ethylcinchoninic acid (IV), m. 180-1.degree.. Samples of III and IV titrated with the aid of a Beckmann pH meter showed that the pH (8.2) at the neutralization point was identical for both acids. The compn.

of the crude mixt. of III and IV obtained in the reaction was estimated to contain about 85% III, as detd. by the m.p. behavior of a series of known mixts. of purified III and IV. II (60 g.), 120 g. PrAc, 200 cc. 34% KOH, and 370 cc. H<sub>2</sub>O gave in the usual manner 81 g. mixed acids, m. beginning at 131.degree., which recrystd. gave the major product, 2-propyl cinchoninic acid, silvery white plates, m. 159.0-9.5.degree.

(decompn.); the crude reaction product (30 g.) recrystd. repeatedly gave 7 g. 3-ethyl-2-methylcinchoninic acid (V), m. above 220.degree., which recrystd. from dioxane gave pure V, white friable powder, m. 257-8.degree. (decompn.); the crude product contained 20-5% V. V heated gave with decarboxylation 3-ethyl-2-methylquinoline (VI), which yielded a picrate, m. 227-30.degree. (decompn.). II (60 g.), 108 g. BuAc, 200 cc. 34% KOH, and 375 cc. H<sub>2</sub>O gave similarly 119 g. crude product, m. beginning at 121.degree., which recrystd. extensively gave 2-butylcinchoninic acid, white friable powder or very fine leaflets, m. 141-2.degree., which was decarboxylated to 2-butylquinoline, identified as the picrate, m. 162.degree.. Fractional extn. of the crude reaction product gave a small amt. of the isomeric 2-methyl-3-propylcinchoninic acid, snow-white powder, m. above 290.degree.

(decompn.). II (60 g.), 105 g. AmAc, 400 cc. 34% KOH, and 900 cc. H<sub>2</sub>O refluxed 78 hrs. with stirring gave similarly 79 g. crude mixed product, m. beginning about 125.degree., which recrystd. repeatedly gave 2-amylcinchoninic acid (VII), m. 135-6.degree. (slight decompn.), previously regarded by Salzer, et al. (C.A. 43, 1415c), as 3-butyl-

2-methylcinchoninic acid (VIII). VII decarboxylated, and the resulting product treated with picric acid gave 2-amyloquinoline picrate, m. 103.0-3.5.degree. (from aq. EtOH). The crude product extd. with dioxane, and the residue from the ext. recrystd. from EtOH gave 3-butyl-2-methylcinchoninic acid, granular white powder, m. 261-3.degree. (decompn.), which constituted only about 5% of the crude product; a sample decarboxylated and treated with picric acid gave 3-butyl-2-methylquinoline picrate, fine yellow needles, m. 210-12.degree. (decompn.). II (50 g.), 75 cc. C<sub>6</sub>H<sub>13</sub>Ac, 180 cc. 34% KOH, and 300 cc. H<sub>2</sub>O refluxed 96 hrs. with stirring gave 82 g. crude product, m. 136-40.degree. (from H<sub>2</sub>O), which recrystd. repeatedly from MeOH gave 2-hexylcinchoninic acid (IX), m. 140-1.degree.. IX decarboxylated and treated with picric acid in MeOH gave 2-hexylquinoline picrate, m. 110-12.degree. (decompn.). 2-Methylcinchoninic acid (8 g.) in 200 cc. H<sub>2</sub>O contg. 2 g. NaOH treated with stirring and heating on a steam cone with 67 g. KMnO<sub>4</sub> in 1200 cc. H<sub>2</sub>O dropwise during 7 hrs., the mixt. heated 70 hrs., treated with a few cc. EtOH to destroy the excess KMnO<sub>4</sub>, and filtered, the clear filtrate concd. to about 500 cc., acidified with HNO<sub>3</sub>, and treated with 200 cc. aq. hot soln. contg. 17 g. Cu(OAc)<sub>2</sub>, the pasty, blue ppt. filtered off, washed with about 500 cc. M AcOH, stirred while being treated with gaseous H<sub>2</sub>S, and filtered, the filtrate evapd. to dryness, the residue (about 2 g.) extd. with hot MeOH, the purplish gel which set to a solid (1.5 g.) powd. and extd. in a Soxhlet app. with EtOAc, and the ext. evapd. gave 2,3,4,6-pyridinetetracarboxylic acid, light tan solid, m. 182-4.degree., expanded to resolidify and then melted with extensive decompn. at about 223-7.degree.. (EtO)<sub>2</sub>CHCOCH<sub>2</sub>CO<sub>2</sub>Et (X) (45 g.) added to 4.8 g. Na in 100 cc. EtOH, the mixt. treated during 70 min. at reflux temp. with 26 g. EtBr, refluxed 13 hrs., and filtered, the filtrate dild. with H<sub>2</sub>O and extd. with Et<sub>2</sub>O, and the ext. dried with Na<sub>2</sub>SO<sub>4</sub> and fractionated gave 38.5 g. (EtO)<sub>2</sub>CHCOCH<sub>2</sub>CO<sub>2</sub>Et (XI), b<sub>5</sub> 118-21.degree., n<sub>20</sub>D 1.4270, d<sub>20</sub> 1.0085, MRD 62.57, 63.61; it gave with aq. FeCl<sub>3</sub> a deep amber color within 1 min. XI (35.5 g.), 145 cc. 2N KOH, and 125 cc. MeOH refluxed 1 hr. with stirring, the MeOH distd. off, the alk. soln. extd. with Et<sub>2</sub>O, and the ext. dried with Na<sub>2</sub>SO<sub>4</sub> and fractionated gave 16.2 g. (EtO)<sub>2</sub>CHCOPr (XII), b<sub>9</sub> 78-9.degree., n<sub>20</sub>D 1.4130, d<sub>20</sub> 0.9187, MRD 47.06; it gave with aq. FeCl<sub>3</sub> during 0.5 hr. a deep golden-brown color. XII treated with KCN and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in aq. EtOH gave 5-diethoxymethyl-5-propylhydantoin, m. 150.degree., XII gave a semicarbazone, m. 244.degree. (decompn.); and a 2,4-dinitrophenylhydrazone, bright orange solid, m. 285-6.degree. (decompn.). XII (10 g.) and 6.35 g. II in 22 cc. aq. alc. KOH and 50 cc. H<sub>2</sub>O refluxed 72 hrs. with stirring, the mixt. cooled, extd. with Et<sub>2</sub>O to recover a small amt. of XII, acidified to ppt. inorg. salt and 3.2 g. II as an agglutinous red mass, and filtered, the filtrate basified with aq. Na<sub>2</sub>CO<sub>3</sub>, concd. to 75 cc. and acidified with concd. HCl, and the resulting spongy, amorphous material crystd. from C<sub>6</sub>H<sub>6</sub> gave 3.3 g. 2-diethoxymethyl-3-ethylcinchoninic acid (XIII), yellowish solid, m. 145-50.degree. (recrystd. from C<sub>6</sub>H<sub>6</sub> and Skellysolve A, fibrous white solid, m. 146.5.degree.). XIII (750 mg.) heated about 4 hrs. with 60 cc. 0.25N H<sub>2</sub>SO<sub>4</sub> on the steam cone, and the soln. concd. and chilled deposited about 500 mg. (88%) material, which recrystd. from hot dil. MeOH gave 3-ethyl-2-formylcinchoninic acid (XIV), white cryst. solid, m. 222-3.degree. (decompn.); it gave a pos. Schiff test for aldehyde. XIV (0.5 g.), 3 g. amalgamated Zn, 12 cc. H<sub>2</sub>O, 3 cc. EtOH, and 15 cc. concd. HCl refluxed 5.5 hrs., the liquid decanted, dild. with an equal vol. H<sub>2</sub>O and sufficient aq. NaOH to ppt. Zn(OH)<sub>2</sub>, and steam distd. to give 100 cc. distillate, the distillate extd. with Et<sub>2</sub>O, the ext. dried and evapd., and the small amt. light brown oily residue treated with picric acid gave the picrate of VI, bright yellow crystals, m. 229.0-9.5.degree. (decompn.); the mother liquor from the

steam distn. gave 200 mg. brown material which could not be purified, since it charred on burning and underwent extensive decompn. at 250-4.degree.; this product was possibly V. X alkylated in the usual manner with BuBr yielded (EtO)2CHCOHBuCO2Et (XV), b. 124-7.degree., n20D 1.4296, d2020 1.001, MRD 71.00; it gave a russet color with aq. FeCl3 within 2 min. XV hydrolyzed with KOH in MeOH gave (EtO)2CHCOAm (XVI), b8-9 94.degree., b. 222.degree., n20D 1.427, d2020 0.912, MRD 56.90, which heated with KCN and (NH4)2CO3 in a sealed tube at 110.degree. yielded 5-amyl-5-(dimethoxymethyl)hydantoin, white crystals, m. 119-20.degree.. XVI did not give with II in alk. soln. a cinchoninic acid. Cl2CHCO2H was converted to (MeO)2CHCO2Et (XVII), b4-5 57-60.degree., n20D 1.4078, d2020 1.054, MRD 34.55. XVII condensed with EtOAc in the presence of Na yielded 76% (MeO)2CHCOCH2CO2Et (XVIII), b4 104.0 .+- 0.5.degree., n20D 1.4286, d2020 1.084, MRD 45.15, which immediately gave a blood-red color when shaken with aq. FeCl3. XVIII gave with H2NCONHNH2.HCl a compd. which was apparently H2NCONHN:CHC(:NNHCONH2)CH2CO2Et, m. 227.degree. with charring. XVIII alkylated with NaOEt and BuBr gave (MeO)2CHCOCHBuCO2Et, b4-5 128.5-9.5.degree., n20D 1.4342, d2020 1.019, MRD 62.90; this sapond. with KOH in MeOH yielded 70% (MeO)2CHCOAm (XIX), b4-5 98-100.degree., n20D 1.4218, d2020 0.939, MRD 47.10. XIX gave a semicarbazone, white crystals, m. 241.2.degree. (decompn.), and a 2,4-dinitrophenylhydrazone, fluffy bright orange powder, m. 185-6.degree.. XIX gave with KCN and (NH4)2CO3 5-amyl-5-(dimethoxymethyl)hydantoin, m. 94-5.degree.. XIX (9 g.), 5.4 g. II, 25 cc. 34% aq. KOH, 45 cc. H2O, and 25 cc. EtOH refluxed 72 hrs. with stirring yielded 8 g. 3-butyl-2-dimethoxymethylcinchoninic acid (XX), m. 155-6.degree. (from C6H6-Skellysolve A). XX (0.75 g.) in 75 cc. 0.4N H2SO4 heated 5 hrs. on the steam bath while adding from time to time small amts. H2O to keep the vol. const., the mixt. cooled, and the resulting crude product (0.6 g., 94%) recrystd. from hot EtOH gave, 3-butyl-2-formylcinchoninic acid, small white crystals, m. 207.degree. (decompn.), gave a pos. Schiff test and a raspberry-red with 2N aq. KOH. XX in aq. EtOH refluxed with concd. HCl and amalgamated Zn, the resulting product dissolved in EtOH contg. NaOH, the soln. refluxed and neutralized, and the tan ppt. recrystd. from aq. EtOH gave 3-butyl-2-methylcinchoninic acid, m. 261-4.degree. with darkening. The substitution of the alkyl groups into the 2-, 3-, or 2,3-positions of cinchoninic acids did not significantly change the max. or min. points of the ultraviolet absorption; the 2-formylcinchoninic acids exhibited a change, evidently due to a lengthening of the conjugation of the unsatn.

L35 ANSWER 11 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1951:36132 HCAPLUS

DN 45:36132

OREF 45:6185a-i,6186a-h

TI The earlier investigations relating to 2-pentenylpenicillin

AU Abraham, E. P.; Baker, W.; Boon, W. R.; Calam, C. T.; Carrington, H. C.; Chain, E.; Florey, H. W.; Freeman, G. G.; Robinson, R.; et al.

CS Princeton Univ. Press

SO Chem. of Penicillin (1949) 10-37

DT Journal

LA Unavailable

CC 10 (Organic Chemistry)

GI For diagram(s), see printed CA Issue.

AB 2-Pentenylpenicillin (I) was recovered from the medium in which it had been produced by a series of extns. with org. solvents. Details of the procedure and of a pilot plant for the recovery are given. The free acid I had the compn. C14-H20N2O4S; Na salt, [.alpha.]20D 305.degree.. I is a monobasic acid, pK approx. 2.9; both N atoms are nonbasic, but after hydrolysis with dil. acid at 100.degree. over 50% of



the total N appears as .alpha.-amino N. When heated at 80.degree. in acid soln. I evolves 2 mols. CO<sub>2</sub>; heating in alk. soln. produces less CO<sub>2</sub>. I with Pd or Pt catalysts takes up 1 mol. of H without loss of antibacterial activity. I Ba salt dissolved in H<sub>2</sub>O (10 mg./ml.) the Ba removed as sulfate, and the soln. let stand at 37.degree. (pH 2) for 3 hrs., followed by extrn. with Et<sub>2</sub>O and concn. of the aq. layer, yields 75% 2-pentenylpenillic acid (II), C<sub>5</sub>H<sub>9</sub>C:N.CH(CO<sub>2</sub>H).CH.N.CH(CO<sub>2</sub>H).CMe<sub>2</sub>.S, m. 165.degree. (decompn.), [.alpha.]<sub>D</sub> 530.degree. (H<sub>2</sub>O, c 0.05%), 455.degree. (0.5 N HCl). Electrometric titration of II showed groups with pK 2.4 and 7.8. In addn. there is an acid group with pK less than 2. Heating to 100.degree. in acid soln. or addn. of HgCl<sub>2</sub> soln. to an aq. soln. of II causes decarboxylation. II heated with 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> (III) in acid soln. yields glyoxal 2,4-dinitrophenylosazone (IV), m. 318.degree. (decompn.) (from pyridine-alc.). II in N HCl shows absorption max. at 2300 A. (E<sub>1</sub>%<sub>1</sub>cm. 200), and at pH 3.3 a max. at 2380 A. (E<sub>1</sub>%<sub>1</sub>cm. 192). II in 0.2 N H<sub>2</sub>SO<sub>4</sub> (100 mg. in 5 ml.) heated in a water bath 1 hr., cooled, brought to pH 6-7 with finely powd. Ba(OH)<sub>2</sub>, the BaSO<sub>4</sub> removed by centrifugation, washed, satd. HgCl<sub>2</sub> soln. added to the supernatant soln., the HgCl<sub>2</sub> complex collected after 30 min., washed with H<sub>2</sub>O, suspended in H<sub>2</sub>O, decompd. by H<sub>2</sub>S, the HgS removed, and the soln. evapd. gave approx. 50 mg. penicillamine-HCl, Me<sub>2</sub>C(SH)CH(NH<sub>2</sub>)CO<sub>2</sub>H.HCl (V. HCl). V.HCl was also prepd. directly from I: I Ba salt was inactivated by letting stand in 0.2 N Ba(OH)<sub>2</sub> (30 mg./ml.) at 37.degree. for 1 hr., the soln. brought to pH 2 with H<sub>2</sub>SO<sub>4</sub>, the BaSO<sub>4</sub> removed, the soln. extd. 3 times with 1/3 its vol. of Et<sub>2</sub>O, the aq. phase adjusted to pH 6, satd. HgCl<sub>2</sub> soln. added, and V.HCl isolated as before (yield, approx. 20 mg. from 100 mg. of I Ba salt of about 1,000 U./mg. activity). V.HCl (100 mg.) in hot Me<sub>2</sub>CO (10 ml.), sepd. from any residue, concd. to 1 ml. by boiling, treated with 1 drop concd. HCl, and cooled yielded 50 mg. isopropylidenepenicillamine-HCl (VI), m. 198.degree., [.alpha.]<sub>D</sub> 94.degree. (H<sub>2</sub>O, c 1%). V.HCl was regenerated by heating at 100.degree. in 0.1 N HCl and evapg. the soln. to dryness in vacuo. V has 3 ionizable groups per N atom, with pK values of 1.8, 7.9, and 10.5, corresponding to the carboxyl, .alpha.-amino, and .beta.-thiol groups. It gives pos. tests for a free SH group with FeCl<sub>3</sub> and with Na nitroprusside. The N appears as .alpha.-amino N (Van Slyke). On treatment with Br-H<sub>2</sub>O the SH group of V is oxidized to SO<sub>3</sub>H; the compd. is called 2-pentenylpenicillaminic acid (VII). VII (14 mg.) dissolved in 0.5 ml. H<sub>2</sub>O, 200 mg. AgNO<sub>2</sub> added, the mixt. treated with 1.14 ml. HCl (d. 1.17) to liberate HNO<sub>2</sub>, allowed to stand in the dark at room temp. for 6 hrs., the AgCl removed by centrifuging, the supernatant soln. and washings evapd. to dryness in vacuo, the thick, oily residue dissolved in H<sub>2</sub>O, the pH adjusted to 7.2 with Ba(OH)<sub>2</sub>, and the soln. evapd. gave 15 mg. of the Ba salt of desaminopenicillaminic acid, C<sub>5</sub>H<sub>9</sub>O<sub>5</sub>NSBa. After removal of the HgCl<sub>2</sub> complex of V in either the acid or alk. prepn. of V, treatment of the supernatant soln. with a soln. of III in 2 N HCl gave a pale yellow cryst. ppt., m. 187-8.degree. (from alc.), of the 2,4-dinitrophenylhydrazone of 2-pentenylpenilloaldehyde (VIII) [60 mg. from 80 mg. II in 4 ml. of 0.2 N H<sub>2</sub>SO<sub>4</sub>, 45 mg. from 160 mg. of I Ba salt in 5.0 ml. of 0.2 N Ba(OH)<sub>2</sub>]. The dimedon deriv. of VIII, m. 161-2.degree. (from 30% aq. alc.), was prepd. from a 10% soln. of dimedon in alc. and an aq. soln. of VIII prepd. from alkali-inactivated I as above. VIII was shown to be (3-hexenoylamino)acetaldehyde by oxidation with Ag<sub>2</sub>O to N-3-hexenoylglycine (IX), m. 110.degree.; Ba salt, m. 212.degree.. Hydrolysis of IX with acid or base for 7 hrs. at 100.degree. (sealed tube) gave glycine; N-(1-naphthylsulfonyl) deriv., m. 150.degree.. Hydrogenation of 20 mg. IX

Ba salt in 1 ml. water over 10 mg. PdCl<sub>2</sub>-C by bubbling H through the soln. gave N-caproylglycine, identical with synthetic material. Identification of EtCHO as a product of the oxidation of IX with cold aq. KMnO<sub>4</sub> established the position of the double bond of the hexenoyl compd. The conclusions were verified by the synthesis of IX and of VIII 2,4-dinitrophenylhydrazone. When 44 mg. II was suspended in water, the pH adjusted to 6 with Ba(OH)<sub>2</sub>, and satd. HgCl<sub>2</sub> soln. added, 1 mole CO<sub>2</sub> was evolved. The ppt., removed by centrifuging, washed, suspended in H<sub>2</sub>O, decompd. with H<sub>2</sub>S, HgS removed, and the supernatant soln. evapd. gave 41 mg. 2-pentenylpenillamine (X), C<sub>5</sub>H<sub>9</sub>-C:N.CH:CH.NCH(CO<sub>2</sub>H)CMe<sub>2</sub>SH, [.alpha.]<sub>D</sub><sup>20</sup> -88.degree.. Oxidation of X with Br-H<sub>2</sub>O gave VII. X. HCl (9.4 mg.) in a few drops of H<sub>2</sub>O, treated with excess Br-H<sub>2</sub>O, then with III in 2 N HCl, gave 5.7 mg. IV. X.HCl (40 mg.) in 4 ml. liquid NH<sub>3</sub>, treated with small pieces of Na until a permanent blue color developed, the color discharged with a crystal of NH<sub>4</sub>Cl, 0.015 ml. PhCH<sub>2</sub>Cl added, the NH<sub>3</sub> evapd., the residue taken up in 1 ml. water, the insol. material centrifuged, the excess PhCH<sub>2</sub>Cl removed by extn. with Et<sub>2</sub>O, and the resulting soln. brought to pH 4 with N HCl gave 40 mg. S-benzyl-2-pentenylpenillamine, m. 128.degree. (from hot water). II in 0.2 N Ba(OH)<sub>2</sub> kept overnight at 37.degree. gave on acidification 25-30% 2-pentenylisopenillic acid (XI), C<sub>5</sub>H<sub>9</sub>C:N.C(CO<sub>2</sub>H):CH.NCH(CO<sub>2</sub>H)C(Me)<sub>2</sub>SH, m. 195-6.degree. (decompn.) (from 70% Me<sub>2</sub>CO). XI gave pos. tests for free thiol; it was not decarboxylated by boiling with 0.1 N HCl for 1 hr. 2-Pentenylpenicillamine disulfide (XII) was prepd. from V by oxidation with air or iodine: 97 mg. V.HCl in 2 ml. water treated with 0.6 ml. N NaOH and a trace of FeCl<sub>3</sub>, shaken for 4 hrs. at 37.degree., and Me<sub>2</sub>CO added to a final concn. of 85% gave 69 mg. XII; 2 ml. V.HCl in 2 ml. H<sub>2</sub>O shaken with 160 mg. iodine in CHCl<sub>3</sub> until no further decolorization occurred, the mixt. sepd., the CHCl<sub>3</sub> washed once with H<sub>2</sub>O, the aq. layers brought to pH 7 with NaOH, and Me<sub>2</sub>CO added to a final concn. of 85% gave 99 mg. XII, m. 160.degree. (decompn.). XII (187 mg.) 1.5 ml. in H<sub>2</sub>O treated with 207 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, the mixt. shaken 12-24 hrs. with addns. of N NaOH to keep the pH above 7, then clarified, by centrifugation, extd. twice with Et<sub>2</sub>O and acidified with N HCl gave 144 mg. bis(p-tolylsulfonyl) deriv. of XII, m. 224-8.degree. (from HOAc). XII was very sol. in H<sub>2</sub>O and was not reduced to the free thiol compd. with KCN, H<sub>2</sub>S, or Sn and HCl. It was not oxidized by the D-.alpha.-amino acid oxidase in kidney nor by the cystine oxidase of liver. On standing in soln. at pH 10 for 15 min. I Na salt lost biol. activity. Treatment of the neutralized soln. with HgCl<sub>2</sub> soln. gave a ppt. of the HgCl<sub>2</sub> complex of V, accompanied by the evolution of CO<sub>2</sub>. The supernatant soln. then gave with III the 2,4-dinitrophenylhydrazone of VIII. The alkali-inactivation product was 2-pentenylpenicilloic acid (XIII), HN.CH(CO<sub>2</sub>H).CMe<sub>2</sub>.S.CHCH(CO<sub>2</sub>R)NHCOC<sub>5</sub>H<sub>9</sub>, R = H. On standing in MeOH, I Na salt became biologically inactive. The product was shown to be .alpha.-Me 2-pentenylpenicilloate (XIV) (XIII, R = Me). XIV with HgCl<sub>2</sub> soln. gave a ppt. of the HgCl<sub>2</sub> complex of V. Addn. of III to the supernatant soln. gave a ppt. of Me 2-pentenylpenaldate 2,4-dinitrophenylhydrazone (XV), m. 146.degree. (from abs. alc.), identical with the 2,4-dinitrophenylhydrazone of Me formyl (3-hexenoylamino)acetate prepd. by the formylation of Me (3-hexenoylamino)acetate with HCO<sub>2</sub>Me and MeONa. I is inactivated by the enzyme penicillinase. The product was shown to be mainly XII. It could be split into V and VII with HgCl<sub>2</sub> soln.

L35 ANSWER 12 OF 15 HCAPLUS COPYRIGHT 2002 ACS

AN 1943:8456 HCAPLUS

DN 37:8456

OREF 37:1424f-i,1425a-i,1426a-b

TI Alstonia alkaloids. I. Degradation of alstonine to .beta.-carboline bases and the reduction of tetrahydroalstonine with sodium and butyl alcohol

AU Leonard, Nelson J.; Elderfield, Robert C.

SO J. Org. Chem. (1942), 7, 556-72

DT Journal

LA Unavailable

CC 10 (Organic Chemistry)

AB A study is made of alstonine (I) from Alstonia constricta. I is isolated according to a modified method (see following abstr.) of Sharp (C. A. 33, 625.1). To establish definitely its empirical formula, C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>, the following salts are prepd.: 2I.H<sub>2</sub>SO<sub>4</sub>.2H<sub>2</sub>O, m. 195-6.degree. and foams 208.degree., [.alpha.]D<sub>25</sub> 127.degree. +- 2.degree. (c 0.492, H<sub>2</sub>O), [.alpha.]D<sub>25</sub> 527.degree.; 2I.H<sub>2</sub>SO<sub>4</sub>.4H<sub>2</sub>O, m. 203-4.degree., [.alpha.]D<sub>25</sub> 120.degree. +- 2.degree. (c 0.548, H<sub>2</sub>O), [.alpha.]D<sub>25</sub> 520.degree.; I.H<sub>2</sub>SO<sub>4</sub>, m. 243-4.degree. (decompn.), [.alpha.]D<sub>25</sub> 120.degree. +- 2.degree. (c 0.588, H<sub>2</sub>O), [.alpha.]D<sub>25</sub> 535.degree.; 2I.H<sub>2</sub>PtCl<sub>6</sub>.H<sub>2</sub>O, m. 220-1.degree. (decompn.); I.HCl, m. 278-9.degree. (decompn.), [.alpha.]D<sub>25</sub> 141.degree. +- 2.degree. (c 0.422, H<sub>2</sub>O), [.alpha.]D<sub>25</sub> 545.degree.; I.HNO<sub>3</sub>, m. 252-4.degree. (decompn.); I.HI, m. 270.degree. (decompn.), and I.HClO<sub>4</sub>, m. 239-40.degree.. Hydrogenation of I in MeOH in the presence of PrO gives tetrahydroalstonine (II), m. 230-1.degree., [.alpha.]D<sub>30</sub> -110.degree. +- 2.degree. (c 0.672, CHCl<sub>3</sub>), [.alpha.]D<sub>27</sub> -88.degree. +- 2.degree. (c 0.412, pyridine). II and yohimbine (III) give in the Adamkiewicz test a blue to violet color which changes to yellow-green, indicating the presence of a tetrahydro-.beta.-carboline ring system in II. I gives only a yellow color. The ultra-violet-absorption curves of II and III are very similar except for an inflection point at about 2500 A. shown by II. When 10 g. I.HCl and 75 g. powd. KOH are fused in a Ni crucible at 300-50.degree. for 1 hr. in a N atm., an insignificant amt. of neutral products and a considerable amt. of acids are formed from which no cryst. compd. is isolated. The basic fraction, amounting to 2.2 g. brown crystals, is purified by chromatographic fractionation, yielding 1.5 g. harman (IV), m. 239-41.degree., which crystallizes in the form of needles and in a more stable form of regular prisms. The picrate of IV m. 257-8.degree. (decompn.), chloroaurate, m. 229.5-30.degree. (decompn.), and benzylidene deriv, m. 204-5.degree.. KOH fusion of 5 g. II under similar conditions gives 350 mg. basic compds., b<sub>0.1-0.15</sub> 140-200.degree. (bath temp.). Their soln. in C<sub>6</sub>H<sub>6</sub> is chromatographed on Al<sub>2</sub>O<sub>3</sub>. Elution of the Al<sub>2</sub>O<sub>3</sub> column with C<sub>6</sub>H<sub>6</sub> and evapn. gives a partially cryst. oil. The crystals, after repeated crystn., give 15 rag. of a base, C<sub>17</sub>H<sub>16</sub>N<sub>2</sub> (V), m. 171.5-2.5.degree.; picrate m. above 267.degree. (decompn.). V gives no color with vanillin-HCl or with Ehrlich's reagent; its alc. soln. shows strong blue fluorescence and is probably a substituted .beta.-carboline. From the oily portion 10 mg. of a sparingly sol. picrate of a base, C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>, m. 261.degree. (decompn. and foaming), is isolated in addn. to a base of the compn. C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>, the picrate of which (15 mg.) m. 203.5-5.5.degree. (decompn.). Elution of the Al<sub>2</sub>O<sub>3</sub> with ether gives 100 mg. IV, m. 238-40.degree., and elution with Me<sub>2</sub>CO gives 10 mg. crude norharman, m. 195.5.degree. after 5 crystns. from C<sub>6</sub>H<sub>6</sub>; its picrate m. 262-3.degree. (decompn.). After extn. with ether, and acidification of the original alk. soln., reextn. with ether gives an ext. which in turn is extd. with H<sub>2</sub>O, 5% NaHCO<sub>3</sub>, 5% Na<sub>2</sub>CO<sub>3</sub> and finally with 10% NaOH. The aq. solns. are acidified and extd. with ether. While from the H<sub>2</sub>O ext. an intractable tar and from the Na<sub>2</sub>CO<sub>3</sub> and NaOH solns. no appreciable amt. is extd., the NaHCO<sub>3</sub> ext. gives a brown oil which is sepd. into 2 fractions, (a) b<sub>0.2</sub> 110-70.degree., (b) b<sub>0.2</sub> above 170.degree. (bath temp.). Fraction a gives 55 mg. colorless plates after recrystn. from C<sub>6</sub>H<sub>6</sub>, m. 205.5-6.degree., and is identical with 2

-indolecarboxylic acid; Me ester, prepd. according to Ciamician and Zatti (Ber. 21, 1929 (1888)), m. 150-1.5.degree.. Thermal decompn. of I by heating 3.6 g. for 1 hr. at 310-60.degree. gives a sublimate which is dissolved in ether and the ether soln. extd. with 10% HCl. Evapn. of the ether leaves a small amt. of neutral material which gives a blue-violet color with Ehrlich's reagent but is not investigated further. From the aq. ext., 3 bases are isolated by fractionated crystn. of their picrates: (c) C17H18N2.C6H3N3O7, yellow monoclinic prisms, m..degree. (decompn.); (d) C18H20N2. or C19H22N2.C6H3N3O7, long yellow needles, m. 193.5-5.degree.; and (e) C13H12N2.C6H3N3O7 (VI), small fine needles, m. 261-2.5.degree. (decompn.). The free base (VII) of VI m. 79-81.degree.; HCl salt turns brown at 227.degree. and decamps. at about 275.degree.; methiodide m. 283-4.degree. (decompn.). As the empirical formula of VII corresponds to an ethyl- or dimethyl-.beta.-carboline, and since its phys. properties show similarity to carboline, 1-ethyl-.beta.-carboline (VIII) is synthesized. N-Nitrosoethylaniline, b17 125-6.degree. is converted into PhNEtNH2 (IX), b13.5 114-16.degree., nD26 1.5642, according to Fischer (Ann. 236, 198(1886)). PhNMeNH2 prepd. in the same way in 52-6% yield b13 106-9.degree.. Benzylidene deriv. of IX m. 49.degree.. When 40 g. H2N(CH2)3CH(OEt)2, b11 85.degree., n 1.4266, prepd. according to Manske (C. A. 25, 4880) and 35 g. IX are condensed in the presence of ZnCl2 and the reaction product is fractionally distd. at 2 mm., 380% 1-ethyltryptamine (X), b2 170-1.degree., nD261.5821, is obtained; its phthalamide m. 149-50.degree.; picrate m. 178.5-80.5.degree.. Treatment of 4 g. X in dil. H2SO4 with HCHO (cf. Spaeth and Lederer, C. A. 24, 2464) gives 1-ethyl-2,3,4,5-tetrahydro-.beta.-carboline (XI), isolated as the picrate in 82% yield, m. 224-5.degree.. XI is not obtained in a cryst. form; its p-nitrobenzamide m. 146-8.degree.. Dehydrogenation of XI with Pd black at 160-70.degree. for 45 min. gives VIII, m. 41-2.degree.; picrate m. 227-8.degree.; methiodide m. 293-5.degree.. VIII is not identical with VII. Norharman-EtI, m. 198-9.degree., when treated with NaOH, gives 3-ethyl-.beta.-isocarboline, m. 176.5-8.5.degree.; ethiodide m. 213.5-15.degree.. Ethiodide of VIII m. 213.5-15.degree.. 2-Ethyl-.beta.-carboline, prepd. by heating tryptophan in dild. H2SO4 with EtCHO, m. 193-5.degree.. Zn distn. of I is carried out in a H atm. and in air at 300-50.degree.. The HCl soln. of the distillate, after being extd. with ether, is made alk. and again extd. with ether. The residue of the ether soln. is twice distd. at 0.2 mm. and 140-80.degree. (bath temp.). The distillate (300 mg.) is dissolved in C6H6 and chromatographed, giving a product the picrate of which m. 261-3.degree. and is identical with VI. Reduction of II with Na in boiling BuOH gives hexahydroalstonine, C20H26N2O2 (XII), m. 282-4.degree. (decompn.), [.alpha.]D27 -78.degree. +- 3.degree. (c 0.338, pyridine); picrate m. 237-8.degree. (decompn.). XII is not obtained on reduction of I under the same conditions. Ac deriv. (XIII) of XII, C22H28N2O3 m. 95-6.degree.; picrate of XIII, m. 223-4.5.degree.. XII has an absorption curve which is identical with that of III and 2,3-dimethylindole. All m. ps. cor. A partial structure for I is discussed.

X L35 ANSWER 13 OF 15 HCAPLUS COPYRIGHT 2002 ACS  
 AN 1923:2093 HCAPLUS  
 DN 17:2093  
 OREF 17:386c-i,387a-b  
 TI Fluorene series. VII. Dibenzofulvene  
 AU Sieglitz, A.; Jassoy, H.  
 SO Ber. (1922), 55B, 2032-40  
 DT Journal  
 LA Unavailable

CC 10 (Organic Chemistry)

AB cf. C. A. 16, 1088 On attempting to decomp. [fluorenyl-9-methyl]-urethan (A),  $(C_6H_4)_2CHCH_2NHCO_2Et$ , into the amine  $(C_6H_4)_2CHCH_2NH_2$ , which it was intended to convert into dibenzofulvene (B),  $(C_6H_4)_2C:CH_2$ , by the Hofmann degradation, S. and J. found to their surprise that 6 g. A distd. with CaO in H under 20-30 mm. yielded directly a small amt. (0.2-0.3 g.) of B, long needles, m. 46-8.degree., quickly decolorizes Br in  $CHCl_3$ , can be recrystd. unchanged from a little MeOH by quick work but on standing the soln. soon becomes turbid and deposits insol. high-melting flocks; the solid B likewise quickly changes, with absorption of O, into amorphous high-melting products; on oxidation it yields fluorenone. Picrate, orange-red, m. 152-3.degree.. In the prepn. of B there remains in the neck of the retort an amber-like insol. resin, softens 255.degree., m. 290.degree., the compn. of which indicates that it is a polymer of B. Ethyl 2,7-dibromo-9-hydroxyfluorene-9-acetate (C), from 2,7-dibromofluorenone (D),  $BrCH_2CO_2Et$  and Zn (etched with HBr) in  $C_6H_6$ , leaves from  $C_6H_6$  or ligroin, m. 106-7.degree., sapond. by hot concd. KOH to the free acid, fine needles from tetralin-PhMe, m. 205-6.degree., sol. in concd.  $H_2SO_4$  with deep red color and yielding on diln. with  $H_2O$  dibromodibenzo-fulvenecarboxylic acid, whose Et ester (E), m. 172-3.degree., is obtained in 13 g. yield by heating at 100.degree. under 18 mm. the C prepd. from 16.7 g. of D; 6.5 g. of the Et 2,7-di-bromofluorene-9-acetate prepd. as described before from E gives when refluxed 12 hrs. with 4.2 g. Of 90%  $N_2H_4$ .  $H_2O$  5 g. of the hydrazide, needles from alc., m. 247-8.degree.; acetone hydrazone,  $C_{18}H_{16}O_2N_2Br_2$ , needles from PhMe, m. 234-5.degree.; benzaldehyde hydrazone, needles from xylene, m. 256-7.degree.. [2,7-Dibromofluorenyl-9-methyl]urethan, from 2 g. of the hydrazide in 40 cc. AcOH cautiously treated with 0.4 g.  $NaNO_2$  in 20 cc.  $H_2O$ , the resulting azide (1.7 g. after drying) being then boiled 8 hrs. with an excess of alc., needles from alc., m. 191-2.degree.. This on distn. with CaO like A above yields neither the amine nor 2,7-dibromobenzofulvene (F), which, however, was obtained as follows: D with MeMgJ in Et<sub>2</sub>O gives 9-methyl-9-hydroxy-2,7-dibromofluorene, Prisms from  $C_6H_6$ , m. 162-3.degree., which in boiling AcOH with concd. HCl yields the 9-methyl-9-chloro derivative, fine needles from alc., m. 182-3.degree.; distn. of this in vacuo does not give F but 9-methyl-2,7-dibromofluorene, m. 136.degree., but the F, fine needles from  $C_6H_6$  or abs. alc., m. 205-6.degree., is obtained when the chloride is boiled 5 min. in AcOH; it quickly decolorizes Br in  $CHCl_3$ , forms in AcOH a clear soln. which after several days deposits insol.flocks, is stable for several days in vacuo, forms no picrate in alc. 9-Ethyl-9-hydroxy-2,7-dibromofluorene, from D and EtMgBr, rodlets or stout prisms from  $C_6H_5$ , m. 133-4.degree.; 9-ethyl-9-chloro compound, needles from alc., m. 171.degree., gives, when refluxed 3 hrs. in AcOH, .omega.-methyl-2,7-dibromodibenzofulvene, woolly needles from AcOH, m. 130-1.degree., decolorizes Br in  $CHCl_3$  and is stable indefinitely. 9-Propyl-9-hydroxy-2,7-dibromo-fluorene, obtained in only 0.3 g. yield, together with higher melting substances, from 1 g. Mg, 3 g. PrBr, 15 cc. Et<sub>2</sub>O and 5 g. D, hard plates from MeOH, m. 150-1.degree.. 2,7-Dibromo-9-hydroxyfluorene, from D with Al-Hg in Moist Et<sub>2</sub>O, needles from AcOH, m. 168.degree.. [9-Benzal-2,7-dibromo-fluorene]-2'-carboxylic acid,  $(C_6H_3Br)_2C:CHC_6H_4CO_2H$  (0.2 g. from 1 g. D and 0.46 g. o-OHCC $C_6H_4CO_2H$  in boiling alc. with 0.5 g. Na), yellow needles from AcOH, softens 218.degree., m. 224.degree.; ethyl ester, felted yellow needles, m. 140.degree.. 3',4'-Dimethox) [9-benzal-2,7-dibromofluorene]2'-carboxylic acid, from opianic acid and D, dull yellow microrodlets from AcOH, m. 249-50.degree.; ethyl ester, deep yellow spears from alc., m. 135.degree., reduced by activated Al in Et<sub>2</sub>O to the dihydro ester, needles from

alc., m. 90.degree..

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AN 1919:7000 HCAPLUS

DN 13:7000

OREF 13:1310f-i,1311a-i,1312a-i,1313a-b

TI .alpha.,.epsilon.-Dialdehydes and .alpha.,.epsilon.-ketoaldehydes, and their conversion into .delta.-lactones. Constitution and method of formation of amaric acid, diethylcarbobenzoic acid and allied compounds

AU Meerwein, Hans; Klinz, Jos.; Dott, Hans

SO J. prakt. Chem. (1918), 97, 225-87

DT Journal

LA Unavailable

CC 10 (Organic Chemistry)

GI For diagram(s), see printed CA Issue.

AB .alpha.,.epsilon.-Dialdehydes and, .alpha.,.epsilon.-ketoaldehydes have been hitherto unknown, with the exception of glutardialdehyde (cf. Harries and Tank, C. A. 2, 2375). Representatives of these 2 classes of compds. can be easily prepd. (1) by addition of desoxybenzoin (a) to .alpha.,.beta.-unsatd. aldehydes:  $\text{PhCH}_2\text{Bz} + \text{RCH:CHCHO} = \text{PhCH(Bz)CH(R)CH}_2\text{CHO}$ , and (2) by addition of  $\text{PhCH}_2\text{CHO}$  to .alpha.,.beta.-unsatd. ketones and aldehydes:  $\text{PhCH}_2\text{-CHO} + \text{RCH:CHCOR}' = \text{Ph(CHO)CHCH(R)CH}_2\text{COR}'$ . A. Addition of desoxybenzoin to .alpha.,.delta.-unsaturated aldehydes. With Jos. Klinz. When 1-2 cc. of a concd. soln. of MeONa in MeOH was added to a mixt. of 132 g. cinnamaldehyde and 19.4 g. of (a) in 80 cc. MeOH at 5 and the mixt. allowed to stand for 2 hrs., 32-5 g. of .beta.-phenyl-.beta.-desylpropionaldehyde (the term "desyl" is applied to the group  $\text{BzCHPh-}$ ),  $\text{BzCHPhCHPhCH}_2\text{CHO}$ , were obtained, fine needles from AcOH, m. 176.5-7.degree., and decomp. on slow heating. Its constitution was proven by its oxidation by means of either  $\text{CrO}_3 + \text{AcOH}$ , or concd.  $\text{HNO}_3 + \text{AcOH}$ , with the formation of the corresponding propionic acid derivative (b), cryst. powder, m. 240-1.degree., which was identical with that described and prepd. according to the method of Klingemann and called by him .beta.-dehydroamaric acid (cf. Ann. 275, 76(1893)). For further confirmation of its structure it was prepd. by the action of (a) in MeOH on Me benzylmalonate and NaOMe, and hydrolysis of the resulting product by boiling with equal parts of AcOH and  $\text{HBr}$ . (b) is converted into .beta.,.gamma.,.delta.-triphenylvalerolactone (.alpha.-amarolactone) by boiling with NaOEt in alc., needles from alc. or AcOEt, m. 140.5-1.degree.. By using KOH in dil. alc., the lactone which forms is hydrolyzed with the formation of .beta.,.gamma.,.delta.-triphenyl-.delta.-hydroxyvaleric acid, needles + 1  $\text{H}_2\text{O}$  from dil. alc., m. 140-5.degree., with re-formation of the lactone. Both the acid and the lactone have been described by Zinin (cf. Jahresber. 30, 81((1877)) under the names amaric acid and amaric anhydride, and their constitutions are now made clear by their formation in the above manner from .beta.-phenyl-.beta.-desylpropionaldehyde. The older name amaric acid is retained, while the lactone is called .alpha.-amarolactone. To distinguish between the 2 stereoisomeric forms, the acid m. 140-5.degree., and giving the lactone m. 141.degree., is called .alpha.-amaric acid. When (b) is reduced with Na-Hg and the product heated in vacuo (to convert it entirely into the lactone) .beta.-amarolactone, m. 168-70.degree., is obtained, which, when dissolved in alc. KOH and then acidified with AcOH, yields .beta.-amaric acid. The latter loses  $\text{H}_2\text{O}$  at 156.degree., giving the original .beta.-lactone, but on oxidation with  $\text{CrO}_3 + \text{AcOH}$  is converted back into (b). The compd. obtained by Klingemann by heating the .alpha.-lactone with 25% alc.  $\text{H}_2\text{SO}_4$  at 100.degree., and m. about 170.degree., is now shown to be anisomeric .gamma.-amaro lactone, which on

oxidation with  $\text{CrO}_3 + \text{AcOH}$  yields  $\gamma$ -amaric acid, lustrous needles, m.  $173^\circ$ . On fusion it is transformed into (b). **EtCH**: $\text{CHMeCHO}$  and (a) in the presence of a little  $\text{NaOMe}$  form  $\alpha$ -methyl- $\beta$ -desylvalerylaldehyde, oil which decomp. s. on heating. It is readily converted by  $\text{NaOMe}$  in  $\text{MeOH}$  into  $\alpha$ -methyl- $\beta$ -ethyl- $\gamma$ ,  $\delta$ -diphenylvalerolactone, large needles, m.  $152^\circ$ . Yield, 78%. In small amts. it bl6  $248-9^\circ$ . By adding cautiously dil.  $\text{H}_2\text{SO}_4$  to the lactone in **alc.**  $\text{NaOH}$  the corresponding hydroxy id is formed, prismatic needles, m.  $136-7^\circ$ . (decompn.). The lactone is identical with the "dipropylcarbобензоник acid" obtained by Zagoumenny (Ann. 184, 166(1877)) by heating (a) with  $\text{KOH}$  in  $\text{PrOH}$  at  $150^\circ$ . Associated with this was an isomeric compd. which M. and K. have now isolated both by Zagoumenny's method and also by heating dipropylcarbобензоник acid with **alc.**  $\text{KOH}$  at  $160^\circ$ . The compd. m.  $152^\circ$  is called  $\alpha$ -dipropylcarbобензоник acid, and the isomer the corresponding  $\beta$ -acid. The latter is dimorphic, forming fine needles and octahedrons, m.  $92-3^\circ$ . On oxidation the  $\alpha$ -acid yields the same  $\alpha$ -methyl- $\beta$ -desylvaleric acid (c) as that obtained by oxidation of the above corresponding aldehyde, fine needles from dil.  $\text{AcOH}$ , m.  $141-3^\circ$ . When it is dissolved in  $\text{NH}_4\text{OH}$ , and  $\text{NaOH}$  is added, an oily sodium salt seps. which on warming changes into an isomeric sodium salt, shining leaves, which on acidifying with  $\text{AcOH}$  yields a stereoisomeric  $\alpha$ -methyl- $\beta$ -desylvaleric acid, m.  $169-71^\circ$ , fine needles. The  $\beta$ -acid, m.  $92-3^\circ$ , on the other hand yields on oxidation another isomeric valeric acid derivative, m.  $184.5-5^\circ$ , prismatic needles which are much more difficultly sol. than the other 2 isomeric acids. On reduction with  $\text{Na-Hg}$  (c) does not yield the original  $\alpha$ -dipropylcarbобензоник acid, but 2 new isomeric lactones,  $\gamma$ -dipropylcarbобензоник acid, m.  $82-4^\circ$  (needles from petr. ether), and the  $\delta$ -acid, m.  $134^\circ$ , needles from **alc.**  $\text{MeCH:CHCHO}$  and (a) yield  $\beta$ -desylbutylaldehyde, oil which decomp. on boiling. Its constitution is shown by its conversion on oxidation into  $\beta$ -desylbutyric acid, needles from **alc.** or  $\text{CS}_2$ , m.  $134-6^\circ$ . It was also prepd. from (a) and  $\text{Me}$  ethylidenemalonate. On warming with 2%  $\text{NaOH}$  it is converted into the isomer (d) (see below), while on boiling it loses  $\text{H}_2\text{O}$  and yields the unsatd. lactone,  $\text{PhCH.CH}_2\text{CO.O.CPh:CPh}$ , lustrous, rhombohedral prisms, m.  $104-6^\circ$ .  $\beta$ -Desylbutylaldehyde is converted by aq.  $\text{KOH}$  into  $\beta$ -methyl- $\gamma$ ,  $\delta$ -diphenylvalerolactone ( $\alpha$ -diethylcarbобензоник acid) (cf. Limpricht and Schwanert, Ann. 155, 66(1870)); Zagoumenny, Ann. 184, 163(1877)), needles from dil. **alc.**, m.  $103-4^\circ$ . On oxidation it yields a  $\beta$ -desylbutyric acid (d), m.  $153.5-4.5^\circ$ , needles from **alc.** The 3rd isomer of this acid obtained by Limpricht and Schwanert, and also by Anschütz and Berns (Ann. 261, 301(1891)), has probably the constitution  $\text{MeCH.CH}_2\text{CO.O.CPhCH}_2\text{Ph}$ .  $\beta$ -Desylpropionaldehyde prepd. from (a) and  $\text{CH}_2\text{:CHCHO}$ , bright yellow oil, which on oxidation gave  $\beta$ -desylpropionic acid in 41% yield (based on the original (a)), long needles m.  $133-4^\circ$  (cf. Knoevenagel, Ber. 21, 1351(1898)). It is not converted by alkalis into a lactone, but on reduction of the aldehyde  $\gamma$ ,  $\delta$ -diphenylvalerolactone is formed (yield quant.), needles from **alc.**, m.  $113-4^\circ$ . B. Addition of phenylvalerolac to  $\alpha$ ,  $\beta$ -unsaturated aldehydes and ketones. With Hans Dott.  $\beta$ ,  $\gamma$ -Diphenylvalerolactone, obtained by the action of  $\text{PhCH}_2\text{CHO}$  on  $\text{PhCH:CHCHO}$  at  $0^\circ$ , then making the mixt. strongly alk. with  $\text{NaOMe}$ , needles +  $1\text{C}_6\text{H}_6$  from  $\text{C}_6\text{H}_6$  + petr. ether, m.  $123-3.5^\circ$ . The intermediate aldehyde was not isolated. Associated with the lactone was a small amt. of a compound m.  $134-6^\circ$ , rhombic plates from  $\text{C}_6\text{H}_6$  + petr. ether. The lactone is readily converted by oxidation with  $\text{KMnO}_4$

into .alpha.,.beta.-diphenylglutaric acid, shining prisms, m. 203-4.degree.; methyl ester, aggregates of needles from dil. alc., m. 84-5.degree.. The above glutaric acid deriv. (cf. Borsche, C. A. 4, 590; Avery and Dole, C. A. 2, 1829) on fusion changes into a stereoisomeric form, m. 231-2.degree. (when quickly immersed in a bath previously heated to 235.degree.). It is best characterized by its methyl ester, prisms from alc., m. 143.degree.; diethyl ester, m. 93-4.degree.. On reduction the above lactone yields .beta.,.gamma.-diphenylvaleric acid, lustrous, prismatic needles from CCl4 + ligroin, m. 109.degree.; sodium salt. By treating the reaction mixt. obtained from PhCH2CHO and PhCH:CHBz at 0.degree. with NaOMe, .alpha.,.beta.,.delta.-triphenyl-.delta.-hydroxyvaleric acid is obtained in 30% yield, lustrous needles from alc. or C6H6 + petr. ether, m. 43-3.5.degree.; sodium salt. Associated with this acid were 2 compounds sol. in Et2O, giving deep red solns. with warm alc. KOH, which on shaking with air are quickly decolorized, the color reappearing on warming. They probably belong to the class of pyranoles. The above OH-acid is readily converted by heating in vacuo at 150.degree. into .alpha.,.beta.,.delta.-triphenylvalerolactone (e), hairy needles from alc., m. 138-9.degree., and when oxidized by KMnO4 yields .alpha.,.beta.,.delta.-triphenyl-.delta.-ketovaleric acid, needles from alc., or AcOH, m. 186-7.degree.; it is purified and isolated in the form of the difficultly sol. methyl ester, long needles from alc., m. 157-8.degree.. An acid of the same **compn.** was obtained by Borsche which m. about 240.degree.. In order to explain the apparent discrepancy in the m. p. it was prepd. by Borsche's method from PhCH2CO2Me and PhCH:CHBz, and 2 isomeric **acids** were obtained, one identical with the above m. 186-7.degree., the other isomer m. 260-1.degree., needles from AcOH. The former partly changes into the latter acid on prolonged heating at 200-20.degree., while some of it loses H2O with the formation of an unsatd. lactone. On reduction with red P and HI, (e) yields .alpha.,.beta.,.delta.-triphenylvaleric acid, PhCH(CO2H)CHPhCH2CH2Ph, needles from alc., m. 174-5.degree.; sodium salt. Like .alpha.-amarolactone (e) is also transformed by mineral acids into an isomeric lactone, prisms + 1 AcOH from AcOH, m. 124.degree.. At 100.degree. in vacuo it loses AcOH and m. 174.degree.. When pptd. from an alk. soln. with dil. H2SO4 it yields an .alpha.,.beta.,.delta.-triphenyl-.delta.-hydroxyvaleric acid (prisms + 1 EtOH from alc., m. 155.degree.), isomeric with the one m. 143-3.5.degree.. .alpha.,.beta.-Diphenyl-.gamma.-carbethoxy-.delta.-ketocapronyl aldehyde, AcCH(EtOCO)CHPhCHPhCHO, prepd. from PhCH2CHO and Et benzalacetate, rhombic tablets + 1 H2O, from dil. alc. It dissolves slowly in alc. KOH, and on acidifying with dil. H2SO4 a thick oil seps. which gives an intense violet color with FeCl3. On distn. in vacuo it decomps., giving AcCH2CO2Et and .alpha.-phenylcinnamyl aldehyde, large crystals from alc., m. 94.degree.. For comparison, the latter was synthesized from PhCH2CHO and BzH; oxime, leaves from alc., m. 165-6.degree.; phenylhydrazone, yellow needles, m. 125-6.degree.. The capronyl aldehyde is converted by 5% alc. HCl at room temp. into a compound, m. 79-81.degree., lustrous prisms from petr. ether, very stable toward alkalis, gives no color with FeCl3, and loses 1 H2O on distn. in vacuo, forming an unsatd. compound, m. 129-30.degree., needles from alc. or Et2O. The compd., m. 79-81.degree., is supposed to be a deriv. of .alpha.,.alpha.-dihydroxytetrahydropyran. C. Addition of anthrone to .alpha.- and .beta.-unsaturated ketones and esters. With Jos. Klinz. Methyl anthronebenzalmalonate prepd. from anthrone and PhCH:C(CO2Me)2 + few drops piperidine, prisms, m. 147.degree.. which on hydrolysis gave .beta.-anthronyl-.beta.-phenylpropionic acid, HO2CCH2CHPhCH.C6H4.CO.C6H4, prisms from alc., m. 195-7.degree.. Ethyl



anthronebenzalacetoacetate, similarly prepd., m. 148-9.degree., needles from alc. Anthrone and PhCH:CHAc likewise gave anthronebenzylideneacetophenone, needles from alc. or AcOH, m. 115-6.degree..

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AN 1917:5530 HCAPLUS

DN 11:5530

OREF 11:1148h-i,1149a-g

TI Attempted scission of racemic alcohols by means of camphoric anhydride

AU Mascarelli, L.; Deliperi, Daria

CS Univ. Cagliari

SO Gazz. chim. ital. (1916), 46(I), 416-30

DT Journal

LA Unavailable

CC 10 (Organic Chemistry)

AB For the theoretical and introductory part of this paper cf. C. A. 11, 789. The attempts to esterify camphoric anhydride with decahydro-.beta.-naphthol were not prolonged owing to anomalies in the reaction. The esterification of PhEtCHOH (a) with camphoric acid and its anhydride was more accurately studied. Tests with PhMeCHOH (b) showed that it reacts the same as (a). Both (a) and (b) were prepd. by Grignard's reaction from BzH. The 1st test was made by fusing (a) with camphoric anhydride (c); secondary products were formed which complicated the sepn. of the unknown esters too much. Heating 6 g. (a) + 2 g. camphoric acid together in a current of HCl gas gave a product partially sol. in alkalis. The sol. part was repptd. with HCl, extd. with petr. ether in order to sep. the product from unchanged camphoric acid. The residue on evapg. the ext. was a dense yellow oil which gave titration values for the .alpha.-mono ester, HO2CC8H14CO2CHEtPh but which (0.3 g.) could not be purified. Boiled under atm. pressure it decomps., giving (c); it is not volatile with steam, its Ba salt darkens at 160.degree. and blackens above 300.degree.. The part insol. in alkalis was extd. with Et2O and when fractionally distd. showed the presence of PhCHClEt which tends to lose HCl in part to give PhCH:CHMe. The distillate is a mixt. of these 2 compds., the latter of which tends to polymerize. Although the expts. were repeated variously no high boiling fraction could be obtained. 4 g. camphoric acid + 15 g. (a) + 5 g. H2SO4 gives a semi-liquid brown mass from which the part sol. in alkalis as above constituted a very poor yield of the mono ester. The part insol. in alkalis was treated as above and the 11 g. of yellow-brown oil fractionated under 34-40 mm. into 8 fractions, the 1st fraction of which consisted mainly of PhCH:CHMe mixed with unchanged (a). The upper fractions correspond in compn. to polymers of PhCH:CHMe. Normal esterification scarcely took place at all with H2SO4; it dehydrates (a) to produce PhCH:CHMe which is polymerized by heat and H2SO4. The simple ether (EtPhCH)2O may also be formed (Oddo, C. A. 5, 2639). Treating Ag camphorate with PhCHClEt for 4-5 hrs. on the H2O bath gave a small yield of the mono ester. The part insol. in alkalis was not studied in detail. 2.6 g. (c) + 10 g. (a) were heated in a sealed tube in a H2O bath for 2 days, or 9 hrs. at 150.degree.. The product was distd. with steam. The part volatile was fractionated and gave 2 slightly d-rotatory fractions and 1 inactive one. The part non-volatile with steam was not fully sepd. into its constituents but the results indicate that much mono ester was present which on distn. gives the neutral ester and camphoric anhydride. 5.2 g. (c) + 20 g. (a) in a sealed tube at 200.degree. for 10 hrs. gave a product entirely sol. in Et2O, which was agitated with dil. NaOH soln. The part sol. in alkalis was repptd. with H2SO4, extd. with petr. ether from

which about 5 g. of impure mono ester was obtained. The part insol. in alkali was fractioned as before; the 1st fractions contained much PhCH:CHMe; the middle fractions contained some unchanged (a) also; the higher fractions contained only (a). The last 2 of the 5 fractions were slightly d-rotatory. This and the previous expt. show that the velocity of esterification of the l-form of (a) is somewhat greater than that of the d-form. The same result was obtained with (b).